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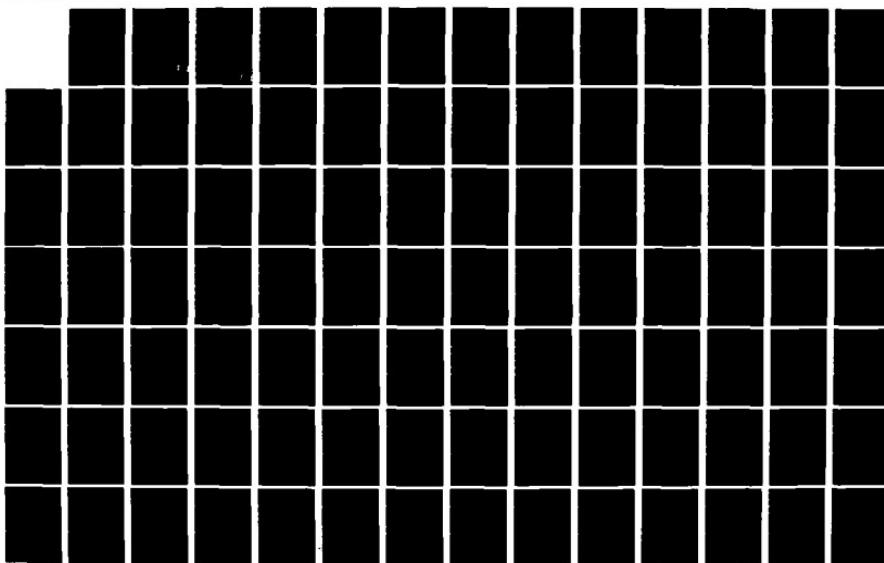
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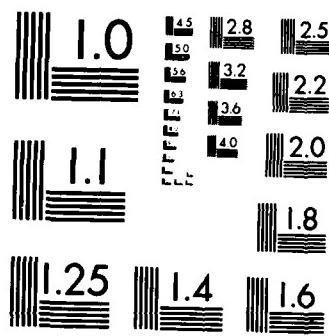
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ANTI-STOKES RAMAN SCATTERING

DISSERTATION

AFIT/DS/PH/82-2

Robert F. Weber
Lt Col USAF

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DISSERTATION

Presented to the Faculty of the School of Engineering
of the Air Force Institute of Technology
Air University
In Partial Fulfillment of the
Requirements for the Degree of
Doctor of Philosophy

By

Robert F. Weber, B.A.A.E., M.S.
Lieutenant Colonel USAF

September 1982



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Preface

They that cannot think, are unfortunate
They that will not, are fools
They that dare not, are slaves

Anonymous

While the work presented in this dissertation must be by necessity and is by desire my own, there are several people to whom I owe a debt of gratitude. First, I would like to thank Mr. Paul Schreiber formerly with the Aero Propulsion Laboratory, Wright-Patterson AFB, Ohio for suggesting this area of research and for introducing me to the field of nonlinear optics. His translation of theory into observable experimental factors was most helpful.

My sincerest appreciation goes to my Advisory Committee for not only keeping me on the right track, but also for just keeping me on the track. Dr Won Roh's numerous discussions on the subject and his willingness to share his time was a key element in understanding the topic. Dr David Lee's mathematical insight helped me see ways to remove several road blocks. I am especially grateful to Dr Alan Garscadden for his continued faith that I could and would complete the research. His understanding of the basic principles and his penetrating questions made our many discussions both enjoyable and rewarding.

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Last, but certainly not least, I thank my wife Bobbie and my family for their understanding, patience and love during this research. It was their confidence and support that enabled me to continue this work to completion. I give a special thank you to my daughter Allison for her help as a proofreader.

Robert F. Weber

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List of Symbols

| <u>Symbol</u> | <u>Definition</u> |
|---------------------------------|--|
| \hat{a} | Unit field vector polarization |
| a^α | Unit field vector polarization component |
| a | Isotropic polarizability invariant |
| $\hat{A}_K^\dagger (\hat{A}_K)$ | Creation (destruction) operator for a photon in mode K |
| $b_{J-K}^{J K}$ | Angular momentum scaling factor for anisotropic polarizability invariant |
| \vec{B} | Magnetic induction vector |
| B_e | Equilibrium constant for rotational energy term equation |
| B_v | Constant for rotational energy term equation with vibrational scaling |
| $\hat{B}_m^\dagger \hat{B}_j$ | Creation (destruction) operator pair for molecule |
| c | Speed of light in a vacuum |
| CARS | Coherent Anti-Stokes Raman Scattering |
| CMRS | Coherent Mixed Raman Scattering |
| CSRS | Coherent Stokes Raman Scattering |
| $\vec{d}(\vec{r},t)$ | Electric dipole moment of a molecule |
| \overline{d}_{ij} | Electric dipole moment matrix element |
| $\frac{d\sigma}{d\Omega}$ | Raman differential scattering cross section per unit solid angle |
| \vec{D} | Electric displacement |
| D_e | Equilibrium constant to account for centrifugal stretching in rotational energy term equation |
| D_v | Constant to account for centrifugal stretching in rotational energy term equation with vibrational scaling |
| \vec{E} | Electric field vector |

List of Symbols

| <u>Symbol</u> | <u>Definition</u> |
|------------------|---|
| E_{rot} | Rotational energy of the molecule |
| E_v | Vibrational energy of the molecule |
| f | Defined notation for a sum of matrix elements |
| \bar{F} | Force |
| g | Defined notation for a sum of matrix elements |
| g_I | Statistical weight due to nuclear spin |
| G | Vibrational energy in wave numbers |
| G_{JK} | Statistical weight due to the degeneracy of the rotational energy level |
| h | Planck's constant |
| \hbar | $\frac{1}{2\pi} h$ |
| \bar{H} | Magnetic field vector |
| \hat{H} | Total Hamiltonian operator |
| \hat{H}_0 | Unperturbed Hamiltonian operator |
| \hat{H}_1 | Perturbation Hamilton operator |
| I | Nuclear Spin |
| I_i | Electromagnetic field (Laser) intensity |
| \bar{J}_s | Surface current density |
| \bar{J} | Electric current density vector |
| J | Quantum number designating rotational energy state |
| \bar{k} | Electromagnetic field propagation vector |
| k | Boltzmann constant |
| m | Reduced mass |
| M | Number of molecules present in the gas |

List of Symbols

| <u>Symbol</u> | <u>Definition</u> |
|-------------------------|--|
| M | Magnetic polarization |
| n | Mean number of photons |
| \hat{n}_{12} | Unit vector normal to a boundary surface |
| N | Number density of molecular per unit volume |
| N.R. | Nonresonant polarizability or susceptibility term |
| \bar{p} | Molecular polarizability |
| P | Electric polarization |
| q | Charge on a single electron |
| Q | Medium response function (temporal) |
| Q_K | Normal coordinate of vibration |
| \bar{r} | Spatial coordinates |
| R | Medium response function (temporal) |
| $R(\theta, \phi, \psi)$ | Rotation matrix |
| SRS-P | Stimulated Raman Scattering - Pump |
| SRS-S | Stimulated Raman Scattering - Stokes |
| SRS-SS | Stimulated Raman Scattering - Second Stokes |
| t | Time coordinate |
| T | Gas temperature |
| $\hat{U}(t)$ | Unperturbed time development operator |
| v | Quantum number designating vibrational energy state |
| V | Volume |
| $V(t)$ | Unperturbed time development operator |
| W | Interaction energy of dipole moment and electric field |
| x | Spatial coordinate component |

List of Symbols

| <u>Symbol</u> | <u>Definition</u> |
|--|--|
| x_e | Anharmonicity constant in vibrational term equation - first order |
| y | Spatial coordinate component |
| y_e | Anharmonicity constant in vibrational term equation - second order |
| z | Spatial coordinate component |
| α | Spatial coordinate index |
| α_e | Vibrational scaling constant for B_V - first order |
| β | Spatial coordinate index |
| β_e | Vibrational scaling constant for B_V - second order |
| γ | Spatial coordinate index |
| γ | Antisotropic polarizability invariant |
| Γ | Linewidth |
| Γ | Damping constant |
| δ | Antisymmetric polarizability invariant |
| δ_{mn}, δ_m^n | Kronecker delta |
| $\delta_i^{\prime}, \delta_i^{\prime\prime}$ | Half width of field component frequency range |
| $\delta(X)$ | Dirac delta function |
| Δ_t | $\rho_{ii}^o - \rho_{jj}^o$ |
| ϵ | Field amplitude in frequency space |
| ϵ' | Dielectric permittivity |
| $\bar{\eta}$ | Magnetic susceptibility |
| θ | Euler angle |
| λ | Anharmonic coefficient |
| μ' | Magnetic permeability |

List of Symbols

| <u>Symbol</u> | <u>Definition</u> |
|--------------------------|--|
| ν | Transition energy of molecule (wave numbers) |
| $\tilde{\nu}$ | Energy of molecular state (wave numbers) |
| $\tilde{\nu}_v$ | Energy of vibrational state divided by ($\nu + 1/2$) |
| $\hat{\xi}$ | Unit field vector polarization |
| ρ | Electric charge density |
| ρ_s | Surface charge density |
| $\hat{\rho}(\vec{r}, t)$ | Density operator |
| ρ_{ii}^o | Matrix element of unperturbed density operator for molecular state i |
| σ | Raman scattering cross section |
| $\bar{\sigma}$ | Specific conductivity |
| τ^{-1} | Transition rate |
| ϕ | Euler angle |
| $\tilde{\chi}$ | Dielectric susceptibility |
| ψ | Molecular wavefunction |
| ψ | Euler angle |
| ω_i | Circular frequency of electromagnetic fields $i = 1, 2, 3, \text{ or } 4$ |
| ω_j | Rotational resonant energy in circular frequency |
| ω_v | Vibrational resonant energy in circular frequency |
| ω_{ij} | $E_i - E_j / \hbar$ |
| Ω | Solid angle measure |
| ∇ | Vector spatial operator |
| S | Symmetrizing operator |
| $\langle \rangle$ | Expectation value |

Abstract

A set of complete and unambiguous third order polarizations were derived for multifrequency (broadband) Coherent Anti-Stokes Raman Scattering (CARS) in molecular gases. The final equations were expressed in a laboratory coordinate frame and were appropriately macroscopic to facilitate the interpretation of experimental results. These polarization equations were made applicable for a general electric field vector polarization and any nonoverlapping distribution of the electric field amplitude in frequency space. The derivation started with the dipole moment approximation and two laser fields as inputs. These two fields, the pump and Stokes fields, had their central frequencies separated by a Raman rotational-vibrational resonant frequency. The generated fields considered were also limited to two; an anti-Stokes and a second Stokes. To more accurately determine the CARS field amplitude, equations were also developed for five related third order nonlinear processes; two parametric (Coherent Stokes Raman Scattering and Coherent Mixed Raman Scattering) and three nonparametric (Stimulated Raman Scattering at the Stokes, pump and second Stokes frequencies). Coherence properties of the fields were not included. The simplification of the general results obtained to the accepted monochromatic equation was noted from the form of the final results.

A semiclassical approach was used in the polarization derivation. Both classical and fully quantized excursions were made where they contributed to the understanding or clarity of the results. Specifically, the induced third order molecular polarizability was

obtained from quantum mechanical perturbation theory. This polarizability was then combined with the electric field present to define the dipole moment of the molecule. By applying classical orientational averaging to a random distribution of molecules, the gas polarization was derived. This derivation was carried out in a laboratory coordinate system and clearly established the role of each polarization vector component. The polarization was defined by the set of equations for each of the six nonlinear processes and the four central frequencies.

From the equations for the polarization, macroscopic susceptibilities were defined that depend on pseudo polarizability invariants. These pseudo polarizability invariants were shown to have the same form as the Raman polarizability invariants. By carefully deriving the molecular Raman differential scattering cross section and establishing the dependence of the average Raman cross section on the same polarizability invariants, the conditions under which the susceptibilities are related to correct Raman scattering cross section were determined.

THIRD ORDER POLARIZATION FOR
MULTIFREQUENCY COHERENT
ANTI-STOKES RAMAN SCATTERING

I. Introduction

Coherent Anti-Stokes Raman Scattering[†] (CARS) is one of the processes caused by the nonlinear coupling or mixing of four electromagnetic (EM) fields by a medium. CARS is used for the spectral analysis of all media; gases, liquids and solids. When it is applied to a molecular gas, macroscopic information (e.g., species concentration and temperatures) and microscopic information (e.g., molecular frequencies and structure) may be obtained. The most common form of CARS developed for this application (Refs 1;2; and 3) uses three intense and nearly monochromatic (narrow band in frequency) EM fields from two separate laser sources at different circular frequencies, ω_1 and ω_2 . The field of greater signal intensity and higher frequency, ω_1 , is called the pump field. It provides two of the photons for the four-wave mixing. The field generated at the slightly lower intensity and lower frequency, ω_2 , is called the idler or for CARS, the Stokes field. It provides a single photon to the process. The Stokes field is produced by a tunable source which allows its frequency to be varied (e.g., a tunable dye laser). When these two intense fields are

[†]CARS is often defined as Coherent Anti-Stokes Raman Spectroscopy. The terminology selected here is to denote the process as opposed to the result.

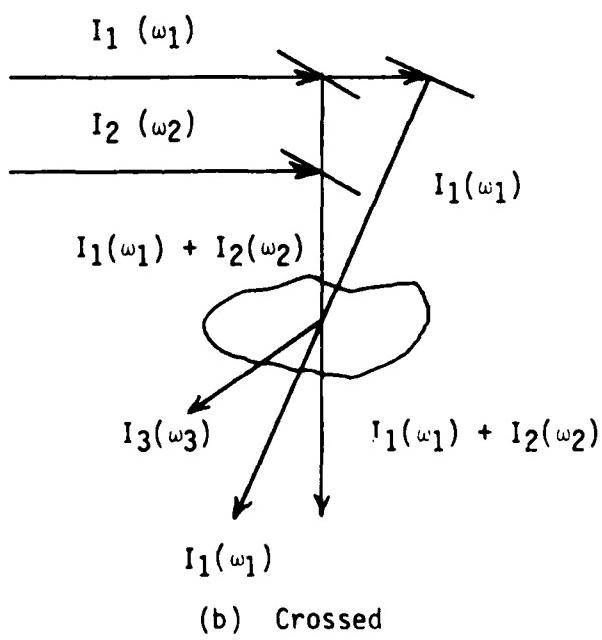
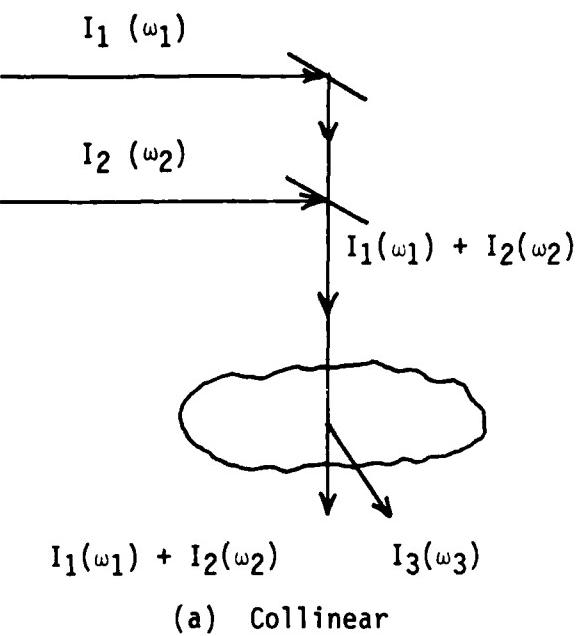


Figure 1. Depiction of Laser Beam Inputs to Generate Third Order Processes

incident on a sample (Figure 1), other fields are generated at different frequencies (e.g., second harmonic, third harmonic, sum and difference fields) and at the same frequencies (e.g., stimulated Stokes field). If the sample under investigation has a Raman active vibration-rotation transition, one of the waves generated at the difference frequency, $\omega_3 = \omega_1 + \omega_1 - \omega_2$, is especially useful when $\omega_1 - \omega_2 \approx \omega_V$ where $\hbar\omega_V$ is the energy corresponding to the Raman active transition. This process and relationship is schematically depicted in Figure 2. The field at the frequency ω_3 is termed the anti-Stokes field. The result of this equality is a resonant enhancement of the amplitude of the anti-Stokes field. Further, the resultant intensity of this wave will produce a Raman spectrum of the molecule as ω_2 is varied. Scattering under these specific conditions is monochromatic CARS. This CARS approach, while highly accurate, does require each experimental point describing the spectrum to be individually generated.

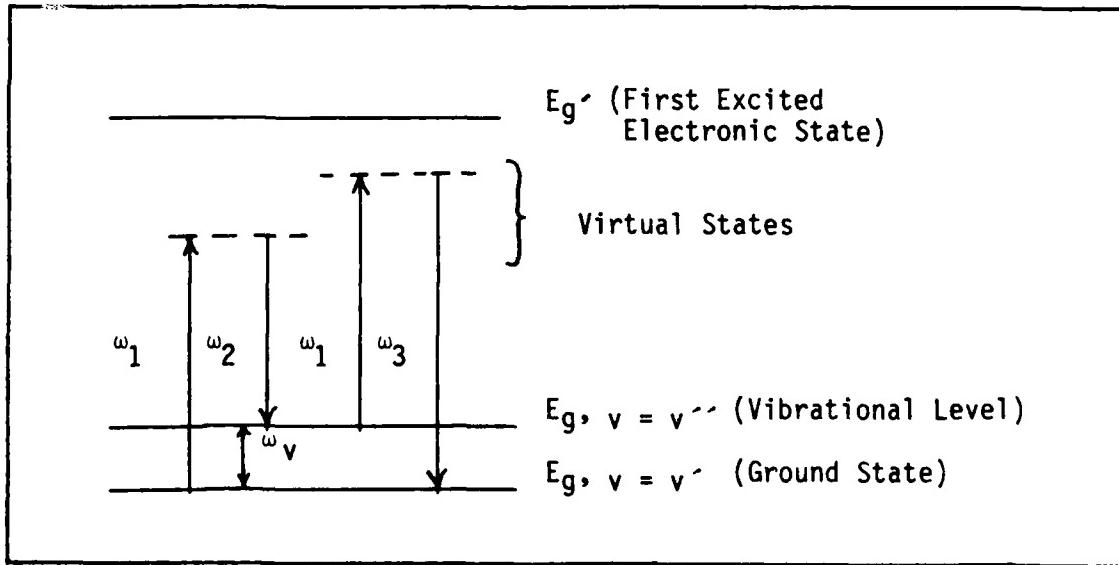


Figure 2. Energy Level Schematic of CARS Process

An alternative CARS technique to the monochromatic one has been developed. This nonmonochromatic approach provides sufficient spectral data in tens of nanoseconds to perform the desired analysis (Refs 4; 5; 6; and 7). This CARS technique has been referred to by several names; single pulse, broad-band, wide bandwidth, multifrequency and multiplex. In the research reported here, the term multifrequency CARS will be used. In the multifrequency CARS approach, a pulsed dye laser is used to produce an intense output over a frequency range sufficient to span several levels of the vibrational Q-branch ($\Delta J = 0$, J denotes the rotational quantum state) of the Raman spectra (of the order $< 200 \text{ cm}^{-1}$). When this multifrequency pulse is used as the Stokes input in CARS, the resultant anti-Stokes output generates the Q-branch spectrum characteristic of the medium. In this way, the real time measurement in a turbulent medium or of other transient effects can be obtained in a medium by using a spectrograph and optical multichannel analyzer.

To adequately describe and predict the spectral characteristics obtained from multifrequency CARS in molecular gases, a complete set of coupled equations for the third order polarization of the nonlinear processes is required. Those nonlinear processes of the same magnitude as CARS are included to determine the effect of intensity and population level saturation on CARS. Since field vector polarization alignment can be used to suppress unwanted background signals and better define the molecular properties, arbitrary alignment of this polarization is also included in the equation for the medium polarization. The orientational averaging of the molecular dipole moments is performed to obtain the polarization terms. This averaging approach,

when applied to the ORS differential cross section, gives a result that eliminates any ambiguity in specifying the correct cross section to be used in CARS and gives the conditions under which the cross sections may be used. From the derived results, the more conventional monochromatic CARS with parallel field vector polarizations is easily obtained.

II. Background and Approach

CARS History

The CARS technique has been receiving ever-increasing attention since it was first used as a diagnostic tool for solids, 1972 (Refs 8; and 9) gases, 1973 (Ref 10; and 11) and liquids, 1974 (Ref 12). However, these first applications of CARS came after many years of studies in inelastic (Raman) and nonlinear scattering which form the basis for CARS. Sir C.V. Raman (Refs 13; and 14) discovered and explained inelastic scattering in 1928. This inelastic scattering which bears Raman's name is that portion of scattered light undergoing a change in frequency characteristic of and determined by the specific scattering molecule. The frequency spectrum of Raman scattered light is thus made up of several lines and the frequency shifts are both positive and negative relative to the incident frequency. When the incident photon loses energy to the scattering molecule by leaving it in an excited state, the frequency shift is negative and the resultant scattered photon is referred to as the Stokes component. When the incident photon gains energy from an encounter with an excited molecule, the frequency shift is positive and the scattered photon is the anti-Stokes component. A theoretical treatment of both Raman and Rayleigh (frequency unchanged or elastic) scattering was prepared by G. Placzek in 1934 (Ref 15) using the quantum theory developed by Dirac to describe the atom or molecule and classical wave theory to describe the electromagnetic fields (this is termed the semiclassical description). In Placzek's work, the "scattering tensor" was obtained and forms the basis for describing Rayleigh and Raman scattering.

This early work is still applicable. From it equations describing hyper, stimulated and electronic Raman scattering (Ref 16) can be obtained. In addition to the work of C. V. Raman and G. Placzek on inelastic scattering, M. Goppert-Mayer (Ref 17) presented an early theoretical treatment of two photon absorption. The early experimental work based on these theories provided a technique that could verify quantum mechanical predictions. However, due to the low efficiency of this scattering phenomena, it was of limited practical application until the development of the laser in the early 1960's. The Raman cross section is several orders of magnitude less than the Rayleigh cross sections (or equivalently absorbtion cross sections). Typically, one Raman photon is scattered for every 10^6 - 10^8 incident photons. With the use of the laser to provide very intense beams the inefficiencies of the Raman process became less important (Refs 18; 19; and 20).

The nonlinear properties of electromagnetic fields are consistent with Maxwell's equations. Several examples of nonlinear effects at lower than optical frequencies have been known for some time (Ref 21). However, it was, also not until the development of the laser that nonlinear properties in the optical region were demonstrated by P. Franken, et.al. (Ref 22) in 1961. Shortly thereafter, R. Terhune and P. Maker (Refs 23; and 24) made the first observation of CARS in liquids. There were several intervening years until the CARS techniques were first developed by J-P Taran and coworkers (Refs 10; and 11) into a practical diagnostic tool. In those intervening years, extensive theoretical work on nonlinear optics was done by several authors; N. Bloembergen (Refs 25-30), P.S. Pershan (Refs 31; and 32),

Y.R. Shen (Refs 33-36), D.A. Kleinman (Ref 37), J. Ducuing (Ref 38), M.D. Levenson (Ref 39; and 40), P.A. Franken (Ref 41), P.D. Maker (Ref 42), and P.N. Butcher (Refs 43-48). While this list is by no means complete, the number of articles does serve to point out the interest placed on the phenomenon. Another reason for selecting these references is that most of this work formed the basis for the CARS theory.

As stated in Chapter I, the anti-Stokes frequency of CARS is a result of just one of the many possible processes that can occur through nonlinear and linear scattering. TABLE I lists several of the scattering processes that are useful in gas diagnostics. These have been described and compared in recent reviews (Refs 49-53). The CARS process, like many of the coherent Raman effects, has some very clear advantages over the noncoherent ones, especially ORS. CARS, due to the resonance at ω_v , has a conversion efficiency of incident light to scattered light that is up to five orders of magnitude greater than that of ORS (Ref 54). This enables easy detection of the scattered intensity both in terms of detector sensitivity as well as time of detection. The intense CARS beam contains the same information as is contained in the weaker ORS output beam so that no information is lost. This has been established by determining that the selection rules are the same for CARS and ORS (Ref 51). A second advantage of CARS arises as a result of the coherent mixing of the two laser beams by the nonlinear susceptibility of the medium and manifests itself as a very low divergent output (the order of 1 mrad). It is this low divergence that also makes detection a simple matter and allows an excellent spatial discrimination. This low divergence combined with

TABLE I
Diagnostic Processes

Non-Coherent

Rayleigh Scattering (RS)
Mie Scattering (MS)
Fluorescence (F)
Two Photon Absorption (TPA)
Ordinary Raman Scattering (ORS)
Near Resonant Raman Scattering (NRRS)
Hyper-Raman Scattering (HRS)

Coherent

Stimulated Raman Scattering (SRS)
Inverse Raman Scattering (IRS)
Coherent anti-Stokes Raman Scattering (CARS)
Coherent Stokes Raman Scattering (CSRS)
Raman Induced Kerr Effect Scattering (RIKES)
Higher Order Raman Spectral Excitation Studies (HORSES)

the frequency shift of ω_3 such that $\omega_3 > \omega_1 > \omega_2$ allows detection against a luminous background. It is this characteristic that makes CARS such a valuable diagnostic tool for combustion processes. The major disadvantage of CARS is the limitation on concentration detection caused by interference effects dependent on nonresonant susceptibilities. This interference may arise for either absolute

concentration in a pure gas or relative concentration in a mixture. The nonresonant susceptibility may be due to either electronic states or adjacent Raman resonant states depending on the energy state characteristics of the specific molecule. The actual level of detection will be a function of pressure and background mixture. The limit on species concentration is typically on the order of 10 ppm. These are only the major advantages and disadvantages of CARS. Several excellent review articles have been written on CARS where a complete discussion of its advantages and disadvantages are discussed (Refs 51; 52; and 54-59).

Just as there are several coherent Raman effects, TABLE I, there are several variations of CARS itself. In addition to the pulsed CARS (multifrequency or narrow frequency), CW CARS has been demonstrated (Ref 60). Also, there are various selections of lasers that can be made to generate the input beams (Ref 56). Different CARS approaches, TABLE II, have also evolved in an attempt to suppress or reduce the nonresonant interference and improve the concentration detectability. The merits of each of these approaches are discussed in several of the reviews (Ref 49;50;59; and 66) and are not repeated here. While the experimental set-up for CARS follows a basic layout (Ref 50), there are as many different ones as there are CARS variations and applications (Refs 51;56; and 67). The specific application of CARS to combustion and gas phase diagnostics is extensively reviewed in a recent article by A. Eckbreth and P. Schrieber (Ref 66). The relatively strong signal levels and coherent property of CARS make it a particularly well suited technique for the measurement of temperature and major concentrations in gases. The use of a multifrequency ω_2 further enhances

the CARS technique in unsteady systems (e.g., turbulent combustion processes) by a time resolved generation of the entire spectrum. It is with this multifrequency application to molecular gases that this research will be concerned.

TABLE II
CARS Background Suppression Techniques

- (1) Resonance Enhancement (Ref 53)
- (2) Double Resonant (Ref 61)
- (3) Polarization (Ref 62)
- (4) Asterisk (Ref 63)
- (5) Background Subtraction (Ref 64)
- (6) Pulse Sequencing (Ref 65)

Approach

In the propagation of electromagnetic fields through a gas, there are two aspects that must be considered: (1) The response of the gas to the electromagnetic field. (2) The evolution of the electromagnetic field in the presence of the gas interaction. These two aspects can be theoretically determined by several approaches. Each aspect may be approached separately from a classical or quantum theoretical point of view. Therefore, the combination of the two effects may be treated strictly classically, quantum mechanically or semi-classically where the material response is obtained using a quantum approach but the fields are described classically. This last approach is followed in this research. The semi-classical treatment is justified where steady state processes are the principal interest

as opposed to detailed information on the generation of photons and where there are a sufficient number of photons making up the fields present. Because of the high intensity of the lasers used, their high degree of coherence and similar properties of the CARS output, this should be a good approximation. This approach will result in the loss of information the contribution of spontaneous emission and statistical fluctuations to the propagation. The fully quantized treatment of several of the nonlinear processes has been performed (Refs 34; and 35). While this treatment is necessary for a full description of the nonlinear phenomena, especially the onset, it adds a high degree of complexity to computations. For diagnostic purposes, there is little return for the added complexity. The quantum approach to the material response presents a different situation. It will be shown that the dielectric susceptibility, $\bar{\chi}^+$, is not only responsible for the magnitude of the resonances present in CARS but also for the specific line shapes and shifts. The source of the resonances and the specific form of the susceptibility are explicitly demonstrated in the quantum approach. The dependence of $\bar{\chi}$ on population difference of molecular states is also clearly shown by this approach. Because of the importance of $\bar{\chi}$ and the need to determine concentrations, the added complexity is felt to be justified for the material response.

For either the quantum or the semiclassical approach, Maxwell's equations, are used to determine the evolution of the EM fields (Ref 68). These equations in Gaussian units are:

[†] The symbol = is used above a parameter throughout to indicate a tensor while the symbols - and ^ are used to indicate an ordinary vector and the unit vector, respectively.

$$\nabla \times \bar{E} = -\frac{1}{c} \frac{\partial \bar{H}}{\partial t} \quad (a)$$

$$\nabla \times \bar{H} = \frac{1}{c} \frac{\partial \bar{E}}{\partial t} + \frac{4\pi}{c} \bar{J} \quad (b) \quad (2.1)$$

$$\nabla \cdot \bar{B} = 0 \quad (c)$$

$$\nabla \cdot \bar{D} = 4\pi\rho \quad (d)$$

where

\bar{E} = electric field vector

\bar{B} = magnetic induction vector

\bar{D} = electric displacement vector

\bar{H} = magnetic field vector

\bar{J} = electric current density

ρ = electric charge density

c = speed of light in a vacuum

t = time dimension

∇ = vector spatial operator (e.g., $\frac{\partial}{\partial x_1} \hat{e} + \frac{\partial}{\partial x_2} \hat{e} + \frac{\partial}{\partial x_3} \hat{e}$)

In addition to these equations, it is necessary to relate the response of the material to the influence of electromagnetic fields. The constitutive relations define the relationships. There are two alternative forms for these relations, additive or multiplicative.

Additive:

$$\bar{D} = \bar{E} + 4\pi\bar{P} \quad (a)$$

$$\bar{B} = \bar{H} + 4\pi\bar{M} \quad (b) \quad (2.2)$$

where

\bar{P} = electric polarization

\bar{M} = magnetic polarization

Multiplicative:

$$\bar{D} = \bar{\epsilon}(\bar{E}) \bar{E} \quad (a)$$

$$\bar{B} = \bar{\mu}(\bar{H}) \bar{H} \quad (b) \quad (2.3)$$

where

$\bar{\epsilon}$ = dielectric permittivity

$\bar{\mu}$ = magnetic permeability

For Eq (2.2)

$$\bar{J} = \frac{\partial \bar{P}}{\partial t} + c \nabla \times \bar{M} \quad (2.4)$$

And for Eq (2.3)

$$\bar{J} = \bar{\sigma} \bar{E} \quad (2.5)$$

where $\bar{\sigma}$ = specific conductivity

For a dielectric (electrical nonconductor), $\sigma \approx 0$, there is no free electric current density and μ and ϵ will completely determine the electric and magnetic properties. Also, for a nonmagnetic material $\mu = 1$. In general, \bar{P} and \bar{M} (or $\bar{\sigma}$, $\bar{\epsilon}$, and $\bar{\mu}$) are functions of the EM fields consistent with the linearity or nonlinearity of the situation.

To solve these equations, certain boundary conditions must also be met. These are summarized as:

$$\begin{aligned}
 \hat{n}_{12} \cdot (\bar{B}_2 - \bar{B}_1) &= 0 & (a) \\
 \hat{n}_{12} \cdot (\bar{D}_2 - \bar{D}_1) &= 4\pi \rho_s & (b) \\
 \hat{n}_{12} \times (\bar{E}_2 - \bar{E}_1) &= 0 & (c) \\
 \hat{n}_{12} \times (\bar{H}_2 - \bar{H}_1) &= \frac{4\pi}{c} \bar{J}_s & (d)
 \end{aligned} \quad (2.6)$$

where

\hat{n}_{12} = unit vector normal to surface between materials 1 and 2 and pointing toward material 2

ρ_s = surface charge density

\bar{J}_s = surface current density

When the external excitation fields are sufficiently weak compared to the molecular internal fields of interaction between charged particles, the external fields do not interact, change their frequency or direction (in a uniform material). The constitutive relations can then be linearized to describe this situation.

$$\bar{P} = \bar{\chi}(\bar{E}, \bar{B}) \bar{E} \longrightarrow \chi \bar{E} \text{ (in uniform medium)} \quad (2.7)$$

$$\bar{M} = \bar{\eta}(\bar{E}, \bar{B}) \bar{H} \longrightarrow \eta \bar{H} \text{ (in uniform medium)} \quad (2.8)$$

where

$\bar{\chi}$ = dielectric susceptibility

$\bar{\eta}$ = magnetic susceptibility

with the result

$$\bar{\epsilon} = 1 + 4\pi \bar{\chi} \quad (2.9)$$

$$\bar{\mu} = 1 + 4\pi \bar{\eta} \quad (2.10)$$

However, in general, this linearization does not hold and the electric polarization has higher order terms that must be taken into account. \bar{P} then may be expanded as

$$\bar{P} = \bar{P}^{(1)} + \bar{P}^{(2)} + \bar{P}^{(3)} + \dots + \bar{P}^{(N)} \quad (2.11)$$

One approximation to obtain the higher order components of \bar{P} is to expand it in a multipole series of the electric and magnetic fields. For a nonpolar and nonmagnetic material, this gives (Ref 42:297)

$$\begin{aligned} \bar{P} = & \bar{x}_1 \bar{E} + \bar{x}_{1a} \nabla \bar{E} + \bar{x}_2 \bar{E} \bar{E} + \bar{x}_{2a} \bar{E} \nabla \bar{E} + \bar{x}_{2b} \bar{B} \frac{\partial \bar{E}}{\partial t} + \\ & + \bar{x}_3 \bar{E} \bar{E} \bar{E} + \bar{x}_{3a} \bar{E} \bar{B} \bar{B} + \dots \end{aligned} \quad (2.12)$$

where $\bar{E} \bar{E}$ is the generalized product of two vectors and \bar{x}_i are tensors of rank $(i + 1)$. In Eq (2.12) the linear part of \bar{P} is

$$\bar{P}^{(1)} = \bar{x}_1 \bar{E} + \bar{x}_{1a} \nabla \bar{E}$$

with the nonlinear terms being the remainder:

$$\text{Second order } \bar{P}^{(2)} = \bar{x}_2 \bar{E} \bar{E} + \bar{x}_{2a} \bar{E} \nabla \bar{E} + \bar{x}_{2b} \bar{B} \frac{\partial \bar{E}}{\partial t}$$

$$\text{Third order } \bar{P}^{(3)} = \bar{x}_3 \bar{E} \bar{E} \bar{E} + \bar{x}_{3a} \bar{E} \bar{B} \bar{B} + \dots$$

For the optical effects discussed in the previous section, a reasonable assumption is that the interaction of the macroscopic field with the material is due to an electric dipole coupling. In the pure electric dipole approximation, Eq (2.12) becomes

$$\bar{P} = \bar{\chi}^{(1)}\bar{E} + \bar{\chi}^{(2)}\bar{E}\bar{E} + \bar{\chi}^{(3)}\bar{E}\bar{E}\bar{E} \quad (2.13)$$

Furthermore, $\bar{\chi}^{(2)}$ is identically zero (Ref 25:9) in an isotropic medium such as a gas which exhibits inversion symmetry in its macroscopic dielectric properties. Thus $\bar{\chi}^{(3)}$ is the lowest order nonlinearity in a gas and $\bar{\chi}^{(3)}$ is the material response function determining CARS as well as the other third order processes of TABLE I. It is through the third order susceptibility term, $\bar{\chi}^{(3)}$, that the Raman resonance must manifest itself. $\bar{\chi}^{(3)}$ must also provide the description of the nonresonant effects, electronic and off-resonant Raman. Thus $\bar{\chi}^{(3)}$ may be written as a sum of these terms

$$\bar{\chi}^{(3)} = \bar{\chi}_r^{(3)} + \bar{\chi}_{nr}^{(3)} \quad (2.14)$$

The generalized product of fields provides the nonlinear nature of the system, and when \bar{E} consists of multiple fields at unique frequencies, many different frequency fields are created. For the third order case, $\bar{E}\bar{E}\bar{E}$, fields having twenty-two distinct frequencies occur when two initial fields are considered. Polarization is induced at each of these frequencies and $\bar{\chi}^{(3)}$, through the induced electric dipole, is a function of the frequencies of the fields it multiplies, e.g., $\bar{\chi}^{(3)}(-\omega; \omega_1, \omega_2, \omega_3)$.

The assumptions that the material is nonmagnetic ($\bar{\mu} = 1$, $\bar{M} = 0$) and that there exists no free charge or current further simplifies the equations. These are good assumptions for gases which are treated in this dissertation. With these assumptions and the use of Eq (2.4), Maxwell's equations become:

$$\nabla \times \bar{E} = - \frac{1}{c} \frac{\partial \bar{B}}{\partial t} \quad (a)$$

$$\nabla \times \bar{B} = \frac{1}{c} \frac{\partial \bar{E}}{\partial t} + \frac{4\pi}{c} \frac{\partial \bar{P}}{\partial t} \quad (b)$$

$$\nabla \cdot \bar{B} = 0 \quad (c)$$

$$\nabla \cdot \bar{D} = 0 \quad (d)$$

$$\bar{P} = \bar{P}_L + \bar{P}^{NL} \quad (e) \quad (2.15)$$

In a dilute medium (such as a gas), the molecules may be treated independently with the microscopic or local field set equal to the applied macroscopic field in these equations. In condensed materials, this latter approximation cannot be made due to the influence of dipoles formed by nearby molecules (Ref 47).

It is clear that by specifying the initial fields the susceptibilities can be obtained under the dipole approximation. This susceptibility can in turn be used to determine the polarization. Equations (2.15) and (2.6) can then accept the polarization to determine the generation and propagation of the electromagnetic fields. This approach will be followed for molecular gas diagnostics by multifrequency CARS. The equations and assumptions of this section will form the basis for this development.

The work of this research is aimed at creating a complete description of the third order polarization for the nonlinear processes (e.g., CARS) under the most general situation for molecular gas diagnostics. The specific objective is to obtain a set of third order polarization equations that will allow the CARS intensity to be

obtained for use in a multifrequency mode to measure the macroscopic parameters of a molecular gas. If the interest were in obtaining information on the structure of molecules, interpretation of the symmetry considerations is necessary (Ref 16:29). Here emphasis will be on using quantum theory to ensure the consistency of the terms in the equations and to accurately express these terms as measurable quantities (e.g., ORS cross sections). To achieve these objectives, arbitrary polarization of the fields[†] will be allowed along with arbitrary dependence of the fields on frequency.

Outline of Contents

The research performed is described in the following six chapters and ten appendices. The majority of these appendices are added for completeness. The remaining appendices are used to consolidate the lengthy and somewhat complex equations for the final results. Because the third order susceptibility is important in defining the polarization, its general properties, including intrinsic permutation symmetry, are derived in Appendix A. With these properties of the susceptibility, the role of the average dipole moment in determining the polarization is established in Chapter III. This chapter also contains the relation between the dipole moment and the nonlinear polarizability. Perturbation theory is used (Appendices B and C) to derive this polarizability for individual molecules. The approach of P.N. Butcher (Ref 48) is followed. The classical derivation of the

[†] N.B. The word polarization is used in two ways; (1) to denote the macroscopic property of the material-electric polarization, and (2) to denote the orientation of the field oscillation in a given frame of reference. The context of use should prevent confusion.

third order susceptibility is outlined for completeness and comparison.

In Chapter IV, the six simultaneous nonlinear processes of the same order of magnitude as CARS are identified. The resonant dipole moment equations for these processes are developed for molecules initially in thermal equilibrium and for a specified field function (Appendix D). The resonant polarizabilities producing the dipole moments are then derived as a set of distinct equations. The results for the six processes are presented in Appendix G in different functional forms. Since one of these forms depends on the ORS polarizability tensor elements, the polarizability invariants are introduced in this chapter. A fully quantized treatment is used to obtain an equation for the molecular ORS differential scattering cross section in Chapter V. The properties of this cross section are reviewed. This derivation and review are performed to ensure the correct use of applicable ORS data from previous experiments reported in the literature.

The effect of averaging over all possible molecular orientations is established in Chapter VI. This orientational averaging allows general field vector polarizations to be considered. The details of this derivation are worked out in Appendix I. In Chapter VII, the orientational averaging result is used to convert the individual molecular dipole moments to a macroscopic polarization and susceptibility. Appendix J contains the equations for the six nonlinear processes of interest. Orientational averaging, similar to that for the polarization, is performed to derive the macroscopic ORS cross section. This clearly shows where an identical substitution of this cross-section

into the third order susceptibility is allowed and where only approximate equality of terms applies. This also allows the importance of the approximations to be determined. Chapter VII concludes with a discussion of other equations and parameters (e.g., line widths) not derived but necessary to solve for the CARS intensity. In the final chapter, VIII, the research results obtained are summarized and recommendations and conclusions presented.

III. Nonlinear Polarization

Quantum Theory

Upon examination of Maxwell's equations, Eq (2.15), the medium polarization term, $\bar{P}(t,r)$, is identified as the parameter connecting the medium response on a macroscopic scale to any applied fields (the term field is understood to be the electromagnetic field). The nonlinear polarization is therefore the forcing function in the derived wave equations for the applied and generated fields. It is also the nonlinear polarization that allows for higher order nonlinear field effects to be incorporated, Eq (2.13). In this chapter, the functional relationship between the polarization and the susceptibility is given. Based upon perturbation theory, the approach to determining the third order susceptibility equations from the average polarizability is established. A classical derivation of this susceptibility is included for completeness and comparison.

Armstrong, et. al. (Ref 26) presents a direct perturbation theory approach similar to that of Kramer (Ref 71:480) to derive certain nonlinear polarization expressions. Recently, other authors (Refs 2;48;72; and 73) have applied perturbation theory through the use of density matrix formalism to derive expressions for the electric susceptibility, \bar{x} . More recently Druet and Taran (Ref 74:8) have reduced the latter approach to a diagrammatic one. In addition to these results, Hellwarth (Ref 75:8) uses the Born-Oppenheimer approximation to separate contributions of the electronic, nuclear and interactive components of the susceptibility. The derivation presented

here will use the density matrix formalism, specifically that of Butcher (Ref 48).

The objective of this research is to obtain an explicit expression for the third order polarization. This is the lowest order of the nonlinear polarization existing for a molecular gas and is used to introduce the CARS effect. The functional definition and general properties of the third order susceptibility are obtained in Appendix A. From this definition, the general third order polarization can be written as

$$\bar{P}^{(3)}(t) = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \bar{x}^{(3)}(\omega_1, \omega_2, \omega_3) \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3) e^{-i(\omega_1 + \omega_2 + \omega_3)t} \quad (A26)$$

or in the terms of the Fourier transform of $\bar{P}^{(3)}(t)$, Eq (A22)

$$\bar{P}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \bar{P}^{(3)}(\tau) e^{i\omega\tau} \quad (3.1)$$

after substituting for $\bar{P}^{(3)}(\tau)$ from Eq (A26).

$$\begin{aligned} \bar{P}^{(3)}(\omega) &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \left[\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \bar{x}^{(3)}(\omega_1, \omega_2, \omega_3) \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3) \right. \\ &\quad \left. \times e^{-i(\omega_1 + \omega_2 + \omega_3)\tau} \right] e^{i\omega\tau} \end{aligned} \quad (3.2)$$

or

$$\bar{P}^{(3)}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \bar{x}^{(3)}(\omega_1, \omega_2, \omega_3) \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3)$$

$$x \int_{-\infty}^{\infty} d\tau e^{i(\omega - \omega_1 - \omega_2 - \omega_3)\tau} \quad (3.3)$$

But, the delta function $\delta(x - x_0)$ is defined by

$$\delta(x - x_0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dy e^{i(x - x_0)y} \quad (3.4)$$

so that the last integral of Eq (3.3) reduces to $\delta(\omega - \omega_1 - \omega_2 - \omega_3)$.

$\bar{P}^{(3)}(\omega)$ is then

$$\bar{P}^{(3)}(\omega) = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \bar{x}^{(3)}(\omega_1, \omega_2, \omega_3) \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3) \delta(\omega - \omega_1 - \omega_2 - \omega_3) \quad (3.5)$$

The principal effort here is to obtain an expression for the polarization or, equivalently, the susceptibility in terms of measurable parameters and thus to link a microscopic derivation to the macroscopic experiment. To perform this derivation, the assumptions of Chapter II and Appendix A will be applied along with the usual relations between the magnetic and electric fields. The electric field in Eq (3.5) is a total field. The applied electric field can be a linear superposition of any number of individual or separate fields. For the case of CARS considered here and the associated third order processes, it is sufficient to allow for two applied fields at (\vec{k}_1, ω_1) and (\vec{k}_2, ω_2) where k_i is the propagation vector. $|\vec{k}_i| = \frac{n_i \omega_i}{c}$ with n_i the index of refraction of the medium at frequency ω_i . The pump electric field, \bar{E}_1 , and the Stokes electric field, \bar{E}_2 , have a functional dependence upon the location, \vec{r} , and time, t .

In deriving an explicit expression for $\chi^{(3)}$, the appropriate starting point is with the definition for the macroscopic polarization (Ref 25:40)

$$\bar{P}(t, \bar{r}) = \frac{M}{V} \langle \bar{d}(t, \bar{r}) \rangle \quad (3.6)$$

where $\bar{d}(t, \bar{r})$ = electric dipole moment of a molecule

V = volume of the gas

M = number of molecules present in the gas

That is, the macroscopic polarization is defined to be a product of the number density and the expectation value of the molecular dipole moment operator, \hat{d} . The expectation value over the correct quantum mechanical system is represented by the symbol $\langle \cdot \rangle$. When the medium under consideration consists of an ensemble of dipole moments that are not uniformly aligned, an appropriate average over all molecular orientations must be taken:

$$\bar{P}(t, \bar{r}) = \frac{M}{V} \overline{\langle \hat{d}(t, \bar{r}) \rangle}^{(\tau)} \quad (3.7)$$

Where the bar over $\langle \hat{d}(t, \bar{r}) \rangle$ indicates orientational averaging.

Placzek and Teller (Ref 76:213) and Ueda and Shimoda (Ref 77:200) have shown the equivalence between classical orientational averaging using the Euler angles and summation over the complete set of orientational quantum numbers. Because of this equivalence, the classical approach will be followed for orientation averaging.

The expectation value of the dipole moment for a single molecule may be obtained by using the density operator, $\hat{\rho}(t)$. For the dipole moment, $\bar{d}(\bar{r})$, at $t = 0$, the expectation value may be written as the

trace

$$\langle \hat{d}(t, \vec{r}) \rangle = \text{Tr} (\hat{\rho}(t) \hat{d}(\vec{r})) \quad (3.8)$$

where Tr is the trace: $(\hat{\rho}(t) \hat{d}(\vec{r}))_{aa} = \sum_a \langle a | \hat{\rho}(t) \hat{d}(\vec{r}) | a \rangle$. In order to find $\hat{\rho}(t)$, it may be expanded as

$$\hat{\rho}(t) = \hat{\rho}_0 + \hat{\rho}_1(t) + \hat{\rho}_2(t) + \hat{\rho}_3(t) + \dots \quad (3.9)$$

so that the trace of the dipole moment is

$$\begin{aligned} \text{Tr}(\hat{\rho}(t) \hat{d}(\vec{r})) &= \text{Tr}(\hat{\rho}_0 \hat{d}) + \text{Tr}(\hat{\rho}_1 \hat{d}) + \text{Tr}(\hat{\rho}_2 \hat{d}) \\ &\quad + \text{Tr}(\hat{\rho}_3 \hat{d}) + \dots \end{aligned} \quad (3.10)$$

The spatial dependence of \hat{d} and the time dependence of $\hat{\rho}$ are suppressed for convenience, but are implied. Equation (3.8) can then be written as

$$\langle \hat{d}(t) \rangle = \langle \hat{d}^{(0)} \rangle + \langle \hat{d}^{(1)}(t) \rangle + \langle \hat{d}^{(2)}(t) \rangle + \langle \hat{d}^{(3)}(t) \rangle + \dots \quad (3.11)$$

where

$$\begin{aligned} \langle \hat{d}^{(0)} \rangle &= \text{Tr}(\hat{\rho}_0 \hat{d}) \\ \langle \hat{d}^{(1)}(t) \rangle &= \text{Tr}(\hat{\rho}_1(t) \hat{d}) \\ \langle \hat{d}^{(2)}(t) \rangle &= \text{Tr}(\hat{\rho}_2(t) \hat{d}) \\ \langle \hat{d}^{(3)}(t) \rangle &= \text{Tr}(\hat{\rho}_3(t) \hat{d}) \\ &\vdots \end{aligned} \quad (3.12)$$

An expression for each order of $\hat{\rho}$ is derived in Appendix B. This derivation is obtained using standard perturbation theory. The interaction picture is used where the Hamiltonian, \hat{H} , is written as

$$\hat{H} = \hat{H}_0 + \hat{H}_1(t) \quad (3.13)$$

where $\hat{H}_1(t)$ represents the perturbation energy introduced by the applied field. In the electric dipole approximation, \hat{H}_1 is given by

$$\bar{H}_1(t) = -\vec{d}(t) \cdot \vec{E}(t) = -d_\alpha(t) E_\alpha(t) \quad (3.14)$$

(Ref 79:265, 80:445). In the last product of Eq (3.14), the Einstein convention is used where repeated indices imply a sum over all values of the index

$$d_\alpha E_\alpha = \sum_{\alpha=1} d_\alpha E_\alpha \quad (3.15)$$

Combining Eqs (3.6) and (3.11), the expectation value of the molecular "third order" dipole moment provides the first step in the derivation of the desired susceptibility. The various orders of $\hat{\rho}$ are used with $\hat{H}_1(t)$ to derive an equation for the expectation value of \hat{d} in Appendix C. From this derivation a molecular polarizability, $\bar{\rho}$, is defined such that

$$\begin{aligned} \langle d_\mu^{(3)}(t, \bar{r}) \rangle &= \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) \\ &\times E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2) E_{\alpha_3}(\omega_3) e^{-i(\omega_1 + \omega_2 + \omega_3)t} \end{aligned} \quad (3.16)$$

where the general form of $p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}$ is given by Eq (C43). Alternatively, the Fourier transform of $\langle d_\mu^{(3)}(t, \bar{r}) \rangle$ is

$$\begin{aligned} \langle d_\mu^{(3)}(\omega) \rangle &= \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau \left[\int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) \right. \\ &\times \left. E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2) E_{\alpha_3}(\omega_3) e^{-i(\omega_1 + \omega_2 + \omega_3)\tau} \right] e^{i\omega\tau} \end{aligned} \quad (3.17)$$

or by rearranging the integrals

$$\langle d_{\mu}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2) E_{\alpha_3}(\omega_3) \\ \times \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{i(\omega - \omega_1 - \omega_2 - \omega_3)} \quad (3.18)$$

After using Eq (3.4), the dipole moment expectation value is

$$\langle d_{\mu}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2) E_{\alpha_3}(\omega_3) \\ \times \delta(\omega - \omega_1 - \omega_2 - \omega_3) \quad (3.19)$$

or

$$\langle \bar{d}_{\mu}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \bar{p}^{(3)}(\omega_1, \omega_2, \omega_3) : \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3) \\ \times \delta(\omega - \omega_1 - \omega_2 - \omega_3) \quad (3.20)$$

when the fields are defined in a laboratory coordinate systems they are independent of the orientational averaging, however, spatial averaging must be performed over the polarizability.

$$\overline{\langle d^{(3)}(\tau) \rangle} = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \overline{\bar{p}^{(3)}}(\omega_1, \omega_2, \omega_3) : \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3) \\ \times \delta(\omega - \omega_1 - \omega_2 - \omega_3) \quad (3.21)$$

Therefore, an expression for the average polarizability is sufficient to determine the susceptibility and consequently the polarization. Substitution of Eqs (3.5) and (3.21) into Eq (3.6) results in the susceptibility, $\chi^{(3)}$ being expressed in terms of the polarizability

$$\bar{\chi}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{M}{V} \overline{\bar{p}^{(3)}}(\omega_1, \omega_2, \omega_3)^{(\tau)} \quad (3.22)$$

To perform the orientational averaging of the polarizability, an explicit expressions for each $\bar{p}^{(3)}(\omega_1, \omega_2, \omega_3)$ of importance to CARS has to be determined.

Classical Theory

A classical development of the nonlinear polarization is an alternative to the quantum derivation in many situations. The classical development starts by considering the interaction of a molecular system with a harmonically oscillating field. A single molecule of the system is assumed to be free to vibrate about the equilibrium position of its nuclei but not to rotate during the interaction. The vibrating molecule can be modeled as a harmonic oscillator

$$\ddot{Q}_k + \Gamma \dot{Q}_k + \omega_v^2 Q_k = \frac{F}{m} \quad (3.23)$$

where

Q_k = a normal coordinate of vibration

Γ = damping constant (proportional to the Raman line width)

ω_v = vibrational resonant frequency

m = reduced mass

F = driving Force

The damping in this equation has been phenomenologically added. Since a molecule placed in an electric field experiences a polarization, \bar{P} , due to the field, a reduction in the energy by

$$W = -1/2 (\bar{P} \cdot \bar{E}) \quad (3.24)$$

results (Ref 84:125). The force, F, associated with this energy is

$$F = -\frac{\partial W}{\partial Q} \quad (3.25)$$

The nonlinear polarization may be obtained using Eqs (3.23), (3.24), and (3.25) in at least two different ways (Ref 2:8):

- (1) Introduction of an anharmonic term, λQ_k^2 , into the oscillator equation of motion through the potential.
- (2) Use of the driving force, F, to introduce the nonlinearity.

This second approach is more commonly used to obtain a classical result and is briefly outlined here. The first approach does produce the following result stated without proof for the polarizability (Ref 2;10)

$$P_{(1)}^{CARS}(\omega_3) = \frac{\lambda^2 q^4 / m}{(\omega_v^2 - \omega_3^2 - i\omega_3\Gamma)(\omega_v^2 - \omega_1^2 - i\omega_1\Gamma)^2 [\omega_v^2 - (\omega_1 - \omega_2)^2 - i(\omega_1 - \omega_2)\Gamma]} \\ \times \frac{1}{(\omega_v^2 - \omega_2^2 + i\omega_2\Gamma)} \quad (3.26)$$

When the driving force is used to introduce the nonlinearity, the relation between the polarization and the applied field is taken to be

$$\bar{P} = \bar{p} \cdot \bar{E} \quad (3.27)$$

where \bar{p} is the polarizability of the molecule induced by the field.

Then \bar{p} is expected to be a function of the nuclear coordinates and each component $p_{\alpha\beta}$ may be written as a Taylor series expansion of the normal vibration coordinates

$$p_{\alpha\beta} = (p_{\alpha\beta})_0 + \sum_k \left(\frac{\partial p}{\partial Q_k} \right)_0 Q_k + \frac{1}{2} \sum_{k,l} \left(\frac{\partial^2 p}{\partial Q_k \partial Q_l} \right)_0 Q_k Q_l + \dots \quad (3.28)$$

where $()_0$ is the value at equilibrium. If only the first order terms in Q are retained and only one normal mode component is assumed as the first approximations, this polarizability becomes

$$p = p_0 + \left(\frac{\partial p}{\partial Q} \right)_0 Q \quad (3.29)$$

where without loss of generality for this approach, \bar{p} is taken as a scalar. Substituting this into Eq (3.27)

$$\bar{P} = (p_0 + \left(\frac{\partial p}{\partial Q} \right)_0 Q) \bar{E} \quad (3.30)$$

and the energy of interaction, W , is

$$W = -\frac{1}{2} [p_0 + \left(\frac{\partial p}{\partial Q} \right)_0 Q] \bar{E} \cdot \bar{E} \quad (3.31)$$

The force F is then

$$F = \frac{1}{2} \frac{\partial}{\partial Q} [p_0 + \left(\frac{\partial p}{\partial Q} \right)_0 Q] \bar{E} \cdot \bar{E} \quad (3.32)$$

$$F = \frac{1}{2} \left(\frac{\partial p}{\partial Q} \right)_0 \bar{E} \cdot \bar{E} \quad (3.33)$$

Upon substitution, Eq (3.23) is

$$\ddot{Q} + \Gamma \dot{Q} + \omega_v^2 Q = \frac{1}{2m} \left(\frac{\partial p}{\partial Q} \right)_0 \bar{E} \cdot \bar{E} \quad (3.34)$$

For the applied field

$$\bar{E} = \bar{E}_1 + \bar{E}_2 \quad (3.35)$$

where \bar{E}_1 and \bar{E}_2 are harmonic fields oscillating at ω_1 and ω_2 respectively,

$$\bar{E}_1 = \bar{\epsilon}_1 e^{i(\bar{k}_1 \cdot \bar{r} - \omega_1 t)} + \text{C.C.} \quad (\text{i})$$

$$\bar{E}_2 = \bar{\epsilon}_2 e^{i(\bar{k}_2 \cdot \bar{r} - \omega_2 t)} + \text{C.C.} \quad (\text{ii}) \quad (3.36)$$

And

$$\bar{E} \cdot \bar{E} = |\bar{E}_1|^2 + 2\bar{E}_1 \cdot \bar{E}_2 + |\bar{E}_2|^2 \quad (3.37)$$

The case where the frequency of the driving force is near the resonant frequency ω_v is important. As before, this resonant condition occurs for

$$\omega_1 - \omega_2 = \omega_v \quad (3.38)$$

and comes from the product of Eq (3.37) with the fields assumed to be parallel

$$\bar{E}_1 \cdot \bar{E}_2 = \epsilon_1^* \epsilon_2^* e^{i[(\bar{k}_1 - \bar{k}_2) \cdot \bar{r} - i(\omega_1 - \omega_2)t]} \quad (3.39)$$

Ignoring the off resonant terms, Eq (3.34) is then

$$\ddot{Q} + \dot{Q} + \omega_v^2 Q = \frac{1}{2m} \left(\frac{\partial P}{\partial Q} \right)_0 2\epsilon_1(\bar{r}) \epsilon_2^*(\bar{r}) e^{-i(\omega_1 - \omega_2)t} + \text{C.C} \quad (3.40)$$

The particular solution to this equation is

$$Q = \frac{1}{2m} \frac{1}{\omega_v^2 - (\omega_1 - \omega_2)^2 - i\Gamma(\omega_1 - \omega_2)} \left(\frac{\partial P}{\partial Q} \right)_0 2\epsilon_1(\bar{r}) \epsilon_2^*(\bar{r}) e^{-i(\omega_1 - \omega_2)t} + \text{C.C.} \quad (3.41)$$

Substituting this value of Q into Eq (3.30) and with the first order correction defined as the nonlinear polarization:

$$\bar{P}^{NL} = \left(\frac{\partial p}{\partial Q} \right)_0 Q \bar{E} \quad (3.42)$$

the result is

$$P^{NL}(\omega_3) = \frac{1}{m} \left(\frac{\partial p}{\partial Q} \right)_0^2 \frac{1}{\omega_v^2 - (\omega_1 - \omega_2)^2 - i\Gamma(\omega_1 - \omega_2)} \epsilon_1^2(\vec{r}) \epsilon_2^* (\vec{r}) \\ \times e^{-i(2\omega_1 - \omega_2)t} \quad (3.43)$$

and

$$P^{NL}(\omega_3) = \frac{1}{m} \left(\frac{\partial p}{\partial Q} \right)_0^2 \frac{1}{\omega_v^2 - (\omega_1 - \omega_2)^2 - i\Gamma(\omega_1 - \omega_2)} \quad (3.44)$$

Similar expressions at other frequencies may also be obtained. The relationship between the term $\left(\frac{\partial p}{\partial Q} \right)_0$ and the Raman differential scattering cross section, $\frac{d\sigma}{d\Omega}$, from ordinary scattering theory is (Ref 85:598)

$$\left(\frac{d\sigma}{d\Omega} \right)_v = \frac{\omega_s^4}{c^4} \left[\left(\frac{\partial p}{\partial Q} \right)_0 Q \right]_{v''}^2 \quad (3.45)$$

where

ω_s = the circular frequency of the scattered radiation.

This differential scattering cross section at vibrational level v can be related to the cross section for scattering from the ground vibrational state, $v=0$ (Ref 86:11), by

$$\left(\frac{d\sigma}{d\Omega} \right)_v = \frac{\omega_s^4}{c^4} \frac{\hbar}{2m\omega_v} \left| \frac{\partial p}{\partial Q} \right|^2 (v+1) \quad (3.46)$$

with

$$\left(\frac{d\sigma}{d\Omega} \right)_v = (v+1) \left(\frac{d\sigma}{d\Omega} \right)_0 \quad (3.47)$$

where the factor $(v+1)$ arises from the dipole matrix element and is introduced into the classical treatment for the transition $v \rightarrow v+1$.

Then

$$\left| \frac{\partial p}{\partial \Omega} \right|^2 = \frac{c^4}{\hbar \omega_s^4} \frac{2m\omega_v}{s} \left(\frac{d\sigma}{d\Omega} \right)_0 \quad (3.48)$$

which upon substitution into equation (3.44) yields

$$p^{NL}(\omega_3) = \frac{2c^4}{\hbar \omega_s^4} \left(\frac{d\sigma}{d\Omega} \right)_0 \frac{\omega_v}{\omega_v^2 - (\omega_1 - \omega_2)^2 - i\Gamma(\omega_1 - \omega_2)} \quad (3.49)$$

The frequency of the scattered radiation, ω_s , should be taken as characteristic of the process being described (e.g., for SRS-S use ω_2).

The tracking of the frequency dependence is difficult in the classical approach since a frequency dependence must be assigned to $(\frac{\partial p}{\partial Q})_0$ (Ref 87:679). A result for CARS at the anti-Stokes frequency (Ref 88) is

$$\left| \frac{\partial p}{\partial Q} \right|^2 = \frac{1}{2} [p'(\omega_1)p'(\omega_3) + p'(\omega_2)p'(\omega_3)] \quad (3.50)$$

where the frequency dependence must be determined and p' is defined as

$$p' = \left(\frac{\partial p}{\partial Q} \right)_0 \quad (3.51)$$

When the field frequencies are far from an electronic state resonance of the molecule, the difference in frequency dependence may be neglected. For the case of CARS, different authors have used both ω_1 and ω_2 to define the frequency dependence and the ω_s of Eq (3.49) (Refs 67:13, and 86:12). The removal of this anomaly is one of the

benefits of the quantum mechanical approach. Schreiber (Ref 88) has obtained the effect of orientational averaging in a molecular gas for the classical derivation under the limiting condition of parallel field polarization.

Selection of Theory

Several considerations must be taken into account in selecting the theory used to derive the nonlinear polarization. Some factors to be considered include the accuracy required, the experimental technique employed (e.g., monochromatic versus multifrequency, electronic resonant enhancement, etc.) and, the purpose of the analysis (e.g., molecular or macroscopic properties). The classical theory result of Eq (3.49) for the nonlinear polarizability and hence the required nonlinear polarization is a good approximation for many of the situations. It is especially useful for those involving only near vibrational resonances. However, the simple classical description is lacking not only for off resonance conditions but also in describing several important features of third order processes.

One of the deficiencies of the simple classical theory is its inability to predict the complete frequency dependence of the polarizability. This frequency dependence is important when describing and differentiating between the third order processes. This is particularly important when electronic state resonances are involved. This frequency dependence arises naturally in the quantum theory. Another deficiency in the classical theory is the inclusion of molecular state population differences and temperature dependence which must be added to the results derived. The damping term, Γ , like

the frequency is analytically included in the quantum approach and occurs in all the frequency dependent terms including those important in electronic resonance. The directional effects arising from field polarization is also described only by the quantum theory through the scattering tensor. The advantages of the quantum theory make it more applicable and worth the slightly more complicated derivations.

For example, if the purpose of the analysis is to determine detailed molecular properties such as symmetry, only the quantum theory will suffice. Even when determining macroscopic properties, such as temperature and pressure, the description by the quantum theory allows a wider range of applications. Also, the classical theory is more difficult to apply to complex molecules.

The quantum theory is, therefore, used to obtain the desired general equations for the molecular polarizability and Raman scattering cross section. Classical orientational averaging is then used to derive the macroscopic susceptibility and polarization with arbitrary field polarization. These can then be used with Maxwell's equations and the appropriate boundary conditions for the most general conditions. This approach is a consistent one to connect the molecular microscopic properties to the experimental macroscopic properties. Specific results such as monochromatic and/or single resonance can be obtained from these general results.

IV. Molecular Polarizability

Dipole Moment Equations

In this chapter, the nonlinear scattering processes of similar magnitude to CARS are identified for the fields present. Third order molecular dipole moment equations are then derived for these processes. The individual resonant polarizabilities that define these dipole moments are then established. An equation for the third order polarizability, $\bar{p}^{(3)}$, is derived in Appendix E from the general form (Appendix C). This derivation uses the unperturbed density operator for molecules in thermal equilibrium. The result is given by Eq (E28) as

$$\begin{aligned}
 p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) = & - \sum_{(\alpha\omega)} \frac{1}{6\hbar^3} \sum_{a,b,c,d} \rho_{aa}^0 \\
 & \times \left[\frac{d_{ab}^\mu d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{ab} + \omega_1 + \omega_2 + \omega_3 + i\Gamma_{ab})(\omega_{ac} + \omega_2 + \omega_3 + i\Gamma_{ac})(\omega_{ad} + \omega_3 + i\Gamma_{ad})} \right. \\
 & + \frac{d_{ab}^{\alpha_1\mu} d_{bc}^{\alpha_2} d_{cd}^{\alpha_3}}{(\omega_{ab} - \omega_1 - i\Gamma_{ab})(\omega_{ac} + \omega_2 + \omega_3 + i\Gamma_{ac})(\omega_{ad} + \omega_3 + i\Gamma_{ad})} \\
 & + \frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^\mu d_{da}^{\alpha_3}}{(\omega_{ab} - \omega_1 - i\Gamma_{ab})(\omega_{ac} - \omega_1 - \omega_2 - i\Gamma_{ac})(\omega_{ad} + \omega_3 + i\Gamma_{ad})} \\
 & \left. + \frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\alpha_3\mu}}{(\omega_{ab} - \omega_1 - i\Gamma_{ab})(\omega_{ac} - \omega_1 - \omega_2 - i\Gamma_{ac})(\omega_{ad} - \omega_1 - \omega_2 - \omega_3 - i\Gamma_{ad})} \right] \quad (4.1)
 \end{aligned}$$

The existence of the frequency resonance in $p^{(3)}$ strongly affects the magnitude. Thus if a specific resonance can be established, the terms

associated with that resonance will dominate. From Chapter I the frequency resonance for CARS is

$$\omega_1 - \omega_2 \approx \omega_v \quad (4.2)$$

where ω_v is identified with ω_{ij} in Eq (3.23). However this resonance will also occur in the polarizabilities for other processes besides that of CARS. The source of the specific linear combinations of frequency in the polarizability is a result of the electric field components present in the total field. This is most clearly seen from an examination of Eq (3.19) where the functional form of the field will restrict the allowed value of ω_i and therefore determine the resonances in $\bar{p}^{(3)}$.

At this point it is necessary to determine the number of field components to be considered. It has been assumed that there are only two real applied fields $\bar{E}_1(t, \bar{r})$ and $\bar{E}_2(t, \bar{r})$ which may be written as

$$\bar{E}_1(t) = \bar{f}_1(t) + \bar{f}_1^*(t) \quad (i) \quad (4.3)$$

$$\bar{E}_2(t) = \bar{f}_2(t) + \bar{f}_2^*(t) \quad (ii)$$

The Fourier transform of the field in this form is carried out in Appendix D with the result

$$\bar{E}_1(\omega) = \bar{\epsilon}_1(\omega) + \bar{\epsilon}_1^*(-\omega) \quad (i) \quad (4.4)$$

$$\bar{E}_2(\omega) = \bar{\epsilon}_2(\omega) + \bar{\epsilon}_2^*(-\omega) \quad (ii)$$

These two fields, interacting through the third order nonlinear polarization term, do create a finite number of electric field

components at new and unequally spaced frequencies. Consider as an example of the applied fields two that are monochromatic at ω_1 and ω_2 so that Eq (4.3) is

$$\bar{E}_1(t, \bar{r}) = \bar{A}_1(\bar{r})e^{-i\omega_1 t} + \bar{A}_1^*(\bar{r})e^{i\omega_1 t} \quad (i)$$

(4.5)

$$\bar{E}_2(t, \bar{r}) = \bar{A}_2(\bar{r})e^{-i\omega_2 t} + \bar{A}_2^*(\bar{r})e^{i\omega_2 t} \quad (ii)$$

and the Fourier transform to frequency space is

$$\bar{E}_1(\omega, \bar{r}) = \bar{A}_1(\bar{r})\delta(\omega - \omega_1) + \bar{A}_1^*(\bar{r})\delta(\omega + \omega_1) \quad (i)$$

(4.6)

$$\bar{E}_2(\omega, \bar{r}) = \bar{A}_2(\bar{r})\delta(\omega - \omega_2) + \bar{A}_2^*(\bar{r})\delta(\omega + \omega_2) \quad (ii)$$

Of the sixty four products obtained in the third order using either Eq (4.5) or (4.6) only six new electric field frequencies and their conjugates will be generated; $3\omega_1$, $2\omega_1 + \omega_2$, $2\omega_2 + \omega_1$, $3\omega_2$, $2\omega_2 - \omega_1$, and $2\omega_1 - \omega_2$. And, of these six only two, $2\omega_1 - \omega_2$ and $2\omega_2 - \omega_1$, will have the resonance of Eq (4.2) occurring in the polarizability. Additional polarizability resonances will exist for field combinations at frequencies of ω_1 and ω_2 such as in a stimulated Stokes process. If the fields generated at the new frequencies, especially those with a resonance, reach a sufficient amplitude, then they in turn can interact with the original fields and each other. This interaction will in turn generate another set of fields at different unequally spaced frequencies. Thus the nonlinear polarization term can in principle create an infinite number of fields at unequally spaced and different frequencies.

In the example just presented, the delta function selects

uniquely the frequencies that will appear in the generated fields and in the polarizability. The polarizability has a single, sharp resonance when Eq (4.2) is satisfied exactly and drops off as the difference increases. The multifrequency situation, in contrast to the monochromatic case, can include a band of frequencies and $E(\omega)$ in Eq (4.4) takes on different functional forms. For well separated fields (i.e., a field is only nonzero over a given frequency band) the functional form of $E(\omega_i)$ and the integration over the entire domain of its argument allows only specific frequencies and thus limits the frequency resonances of the polarizability. Only certain of the twenty four terms in Eq (4.1) contain a resonance at $\omega_1 - \omega_2$ and the selection of the resonance limits the number of separate terms that must be considered. The remainder of the terms (i.e., those not in resonance) are included in the nonresonant background polarizability. To determine the resonant polarizability terms, the field terms will be limited to the applied fields E_1 and E_2 and to the generated fields \bar{E}_3 (at $\omega_3 = \omega_1 + \omega_1 - \omega_2$) and \bar{E}_4 (at $\omega_4 = \omega_2 + \omega_2 - \omega_1$). This is not only consistent with experimental observation (Ref 81:145) where gas breakdown limits the intensities precluding generation of detectable higher order fields but is also sufficient to describe the processes important to CARS. Then Eq (3.20) with Eq (4.3) becomes

$$\begin{aligned} \langle d^{(3)}(\omega) \rangle &= \sum_{i,j,k=1}^4 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' \bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') \\ &\times [\bar{\epsilon}(\omega') + \bar{\epsilon}^*(-\omega')]_i [\bar{\epsilon}(\omega'') + \bar{\epsilon}^*(-\omega'')]_j [\bar{\epsilon}(\omega''') + \bar{\epsilon}^*(-\omega''')]_k \\ &\times \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (4.7)$$

where the notation change

$$\begin{aligned}\omega_1 &\rightarrow \omega' \\ \omega_2 &\rightarrow \omega'' \\ \omega_3 &\rightarrow \omega'''\end{aligned}$$

has been made to avoid confusion with the specific frequencies such as the pump frequency ω_1 . The Bloembergen notation $p^{(3)}(-\omega; \omega', \omega'', \omega''')$ has been used for the polarizability term. The expansion of the field terms on the right hand side (RHS) of this equation is

$$\begin{aligned}[\bar{\epsilon}(\omega') + \bar{\epsilon}^*(-\omega')]_i [\bar{\epsilon}(\omega'') + \bar{\epsilon}^*(-\omega'')]_j [\bar{\epsilon}(\omega''') + \bar{\epsilon}^*(-\omega''')]_k = \\ \bar{\epsilon}_i(\omega') \bar{\epsilon}_j(\omega'') \bar{\epsilon}_k(\omega''') + \bar{\epsilon}_i^*(-\omega') \bar{\epsilon}_j(\omega'') \bar{\epsilon}_k(\omega''') \\ + \bar{\epsilon}_i(\omega') \bar{\epsilon}_j^*(-\omega'') \bar{\epsilon}_k(\omega''') + \bar{\epsilon}_i(\omega') \bar{\epsilon}_j(\omega'') \bar{\epsilon}_k^*(-\omega''') \\ + \bar{\epsilon}_i^*(-\omega') \bar{\epsilon}_j^*(-\omega'') \bar{\epsilon}_k^*(-\omega''') + \bar{\epsilon}_i(\omega') \bar{\epsilon}_j^*(-\omega'') \bar{\epsilon}_k^*(-\omega''') \\ + \bar{\epsilon}_i^*(-\omega') \bar{\epsilon}_j(\omega'') \bar{\epsilon}_k^*(-\omega''') + \bar{\epsilon}_i^*(-\omega') \bar{\epsilon}_j^*(-\omega'') \bar{\epsilon}_k(\omega''') \quad (4.8)\end{aligned}$$

The last four terms in this equation are complex conjugates of the first four terms. When used in the wave equation they will form a set of conjugate equations and may be treated as providing redundant information. Using these results, Eq (4.7) becomes

$$\begin{aligned}
\langle \bar{d}^{(3)}(\omega) \rangle &= \sum_{i,j,k=1}^4 \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''')] \\
&\quad : \hat{a}_i \hat{a}_j \hat{a}_k \epsilon_i(\omega') \epsilon_j(\omega'') \epsilon_k(\omega''') \\
&\quad + \bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_i^* \hat{a}_j \hat{a}_k \epsilon_i^*(-\omega') \epsilon_j(\omega'') \epsilon_k(\omega''') \\
&\quad + \bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_i \hat{a}_j^* \hat{a}_k \epsilon_i(\omega') \epsilon_j^*(-\omega'') \epsilon_k(\omega''') \\
&\quad + \bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_i \hat{a}_j \hat{a}_k^* \epsilon_i(\omega') \epsilon_j(\omega'') \epsilon_k^*(-\omega''') + \text{C.C.}] \\
&\quad \times \delta(\omega - \omega' - \omega'' - \omega''')
\end{aligned} \tag{4.9}$$

Where the field term has been divided into a product of a unit vector, \hat{a}_i , denoting the field spatial polarization and the scalar function $\epsilon_i(\omega)$. By allowing the unit vector to be complex, the field polarization may be other than linear.

For each of the four triple products in Eq (4.9), there are sixty four terms and for each $\bar{p}^{(3)}$ there are twenty four terms due to the symmetrizing operator, S , in Eq (4.1). A reduction in this number of terms to those of interest is possible by using the property of intrinsic permutation symmetry from Appendix C, keeping only the resonant terms of $\bar{p}^{(3)}$, and using the localization property of the field amplitude distribution function in frequency space. A brief description of how the three effects are used to derive the resonant terms is given. In each of the sixty four product terms, the individual field functions can occur with a permuted order. For example, in the first term on the RHS of Eq (4.9) the terms with indices 1,1,2 are

$$\begin{aligned}
 \epsilon_1(\omega')\epsilon_1(\omega'')\epsilon_2(\omega''') & \quad (i) \\
 \epsilon_1(\omega')\epsilon_2(\omega'')\epsilon_1(\omega''') & \quad (ii) \\
 \epsilon_2(\omega')\epsilon_1(\omega'')\epsilon_1(\omega''') & \quad (iii) \quad (4.10)
 \end{aligned}$$

and may all occur. The number of individual products containing the same set of indices may be predicted from the following expression:

$$\frac{\text{Number of ways first field chosen} \times \text{Number of ways second field chosen} \times \text{Number of ways third field chosen}}{(\text{number of terms alike})!} \quad (4.11)$$

In the example above, since there is nothing to distinguish the individual field functions (e.g., no conjugation on one of the terms), the first field may be chosen in three different ways. The second field may then be chosen in either of two ways and the third field in only one way. There are two field indices alike. Equation (3.33) then becomes

$$\frac{(3) \times (2) \times (1)}{2!} = 3$$

In the remainder of terms on the RHS of Eq (4.9), one field is conjugated and since that field is identified by a subscript it can only be chosen one way. The number of similar subscripted field products will be either one or two depending on the number of terms alike, two or one. Once the number of field product terms with like indices is known, the combining of these is possible using the intrinsic permutation symmetry. This is best demonstrated using the field products of Eq (4.10). The polarizability expressions are

$$\left[\int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu \alpha_1 \alpha_2 \alpha_3}^{(3)}(\omega', \omega'', \omega''') a_1^{\alpha_1} a_1^{\alpha_2} a_2^{\alpha_3} \epsilon_1(\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \right]_{(i)}$$

$$+ \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu \alpha_1 \alpha_2 \alpha_3}^{(3)}(\omega', \omega'', \omega''') a_1^{\alpha_1} a_2^{\alpha_2} a_1^{\alpha_3} \epsilon_1(\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \right]_{(ii)}$$

$$+ \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu \alpha_1 \alpha_2 \alpha_3}^{(3)}(\omega', \omega'', \omega''') a_2^{\alpha_1} a_1^{\alpha_2} a_1^{\alpha_3} \epsilon_2(\omega') \epsilon_1(\omega'') \epsilon_3(\omega''') \right]_{(iii)}$$

$$x \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.12)$$

where a^α and ϵ are scalars. Expression (iii) in Eq (4.12) may be rewritten by first switching the dummy indices α_1 and α_2 and relocating the scalar components

$$\int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu \alpha_1 \alpha_2 \alpha_3}^{(3)}(\omega', \omega'', \omega''') a_1^{\alpha_1} a_2^{\alpha_2} a_1^{\alpha_3} \epsilon_2(\omega') \epsilon_1(\omega'') \epsilon_3(\omega''')$$

$$x \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.13)$$

Since the variables ω' and ω'' are under the integral, they may also be switched along with the order of integration and the scalar fields relocated

$$\int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu \alpha_1 \alpha_2 \alpha_3}^{(3)}(\omega'', \omega', \omega''') a_1^{\alpha_1} a_2^{\alpha_2} a_1^{\alpha_3} \epsilon_1(\omega') \epsilon_2(\omega'') \epsilon_3(\omega''')$$

$$x \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.14)$$

Use the intrinsic permutation property of $\bar{p}^{(3)}$

$$p_{\mu \alpha_2 \alpha_1 \alpha_3}^{(3)}(\omega'', \omega', \omega''') = p_{\mu \alpha_1 \alpha_2 \alpha_3}^{(3)}(\omega', \omega'', \omega''') \quad (4.15)$$

to obtain

$$\int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega', \omega'', \omega''') a_1^{\alpha_1} a_2^{\alpha_2} a_3^{\alpha_3} \epsilon_1(\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \\ \times \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.16)$$

which is exactly Expression (4.12ii). Expression (4.12i) may be rewritten in a similar manner by exchanging indices α_2 and α_3

$$\int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu\alpha_1\alpha_3\alpha_2}^{(3)}(\omega', \omega'', \omega''') a_1^{\alpha_1} a_2^{\alpha_2} a_3^{\alpha_3} \epsilon_1(\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \\ \times \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.17)$$

exchange the variables ω'' and ω''' as before

$$\int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu\alpha_1\alpha_3\alpha_2}^{(3)}(\omega', \omega''', \omega'') a_1^{\alpha_1} a_2^{\alpha_2} a_3^{\alpha_3} \epsilon_1(\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \\ \times \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.18)$$

From intrinsic permutation symmetry of $\bar{p}^{(3)}$

$$p_{\mu\alpha_1\alpha_3\alpha_2}^{(3)}(\omega', \omega''', \omega'') = p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega', \omega'', \omega''')$$

and Expression (4.18) becomes

$$\int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega', \omega'', \omega''') a_1^{\alpha_1} a_2^{\alpha_2} a_3^{\alpha_3} \epsilon_1(\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \\ \times \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.19)$$

which is also Expression (4.12ii). Therefore, all three terms in Expression (4.12) are identical so that the number of like terms beco-

mes a coefficient to one of the terms. In this case, a factor of three. Following a similar procedure, this result can be obtained for each of the terms in Eq (4.9).

Equation (4.1), after expanding to obtain explicitly the density of states, can be used to determine the resonant terms in $\tilde{p}^{(3)}$. Also, because of the resonant requirement of Eq (4.2) and the inclusion of the four fields with amplitude distribution functions (frequency components of the field) localized about ω_1 , ω_2 , $\omega_3 = 2\omega_1 - \omega_2$ and $\omega_4 = 2\omega_2 - \omega_1$ in frequency space, only the denominator terms

$$\begin{aligned} & \omega_{ac} + \omega'' + \omega''' + i\Gamma_{ac} \\ & \omega_{ac} - \omega' - \omega'' - i\Gamma_{ac} \end{aligned} \quad (4.20)$$

of Eq (4.1) can result in resonance. Thus, Eq (4.1) can be expanded by performing the summations over a and c to the desired level. For the case of interest here, only those adjacent vibrational states need to be considered with the result:

$$p_{\mu\alpha}^{(3)} \propto (-\omega; \omega', \omega'', \omega''') = - \sum_{(\alpha\omega)} \frac{1}{6\hbar^3} \sum_{b,d} \rho_{00}^0$$

$$\times \left[\frac{d_{ob}^\mu d_{b1}^{\alpha_1} d_{1d}^{\alpha_2} d_{do}^{\alpha_3}}{(\omega_{ob} + \omega' + \omega'' + \omega''' + i\Gamma_{ob})(\omega_{o1} + \omega' + \omega'' + i\Gamma_{o1})(\omega_{od} + \omega''' + i\Gamma_{od})} \right] \quad (i)$$

$$+ \frac{d_{ob}^{\alpha_1} d_{b1}^\mu d_{1d}^{\alpha_2} d_{do}^{\alpha_3}}{(\omega_{ob} - \omega' - i\Gamma_{ob})(\omega_{o1} + \omega'' + \omega''' + i\Gamma_{o1})(\omega_{od} + \omega''' + i\Gamma_{od})} \quad (ii)$$

$$+ \frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_2} d_{1d}^\mu d_{do}^{\alpha_3}}{(\omega_{ob} - \omega' - i\Gamma_{ob})(\omega_{o1} - \omega' - \omega'' - i\Gamma_{o1})(\omega_{od} + \omega''' + i\Gamma_{od})} \quad (iii)$$

$$+ \frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_2} d_{1d}^{\alpha_3} d_{do}^\mu}{(\omega_{ob} - \omega' - i\Gamma_{ob})(\omega_{o1} - \omega' - \omega'' - i\Gamma_{o1})(\omega_{od} - \omega' - \omega'' - \omega''' - i\Gamma_{od})} \Big]_J \quad (iv)$$

$$+ \rho_{11}^0 \left[\frac{d_{1b}^\mu d_{bo}^{\alpha_1} d_{od}^{\alpha_2} d_{d1}^{\alpha_3}}{(\omega_{1b} + \omega' + \omega'' + \omega''' + i\Gamma_{1b})(\omega_{10} + \omega' + \omega''' + i\Gamma_{10})(\omega_{1d} + \omega''' + i\Gamma_{1d})} \right] \quad (v)$$

$$+ \frac{d_{1b}^{\alpha_1} d_{bo}^\mu d_{od}^{\alpha_2} d_{d1}^{\alpha_3}}{(\omega_{1b} - \omega' - i\Gamma_{1b})(\omega_{10} + \omega'' + \omega''' + i\Gamma_{10})(\omega_{1d} + \omega''' + i\Gamma_{1d})} \quad (vi)$$

$$+ \frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_2} d_{od}^\mu d_{d1}^{\alpha_3}}{(\omega_{1b} - \omega' - i\Gamma_{1b})(\omega_{10} - \omega' - \omega'' - i\Gamma_{10})(\omega_{1d} + \omega''' + i\Gamma_{1d})} \quad (vii)$$

$$+ \frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_2} d_{od}^{\alpha_3} d_{d1}^\mu}{(\omega_{1b} - \omega' - i\Gamma_{1b})(\omega_{10} - \omega' - \omega'' - i\Gamma_{10})(\omega_{1d} - \omega' - \omega'' - \omega''' - i\Gamma_{1d})} \quad (viii)$$

$$+ \frac{d_{1b}^\mu d_{b2}^{\alpha_1} d_{2d}^{\alpha_2} d_{d1}^{\alpha_3}}{(\omega_{1b} + \omega' + \omega'' + \omega''' + i\Gamma_{1b})(\omega_{12} + \omega' + \omega''' + i\Gamma_{12})(\omega_{1d} + \omega''' + i\Gamma_{1d})} \quad (ix)$$

$$+ \frac{d_{1b}^{\alpha_1} d_{b2}^u d_{2d}^{\alpha_2} d_{d1}^{\alpha_3}}{(\omega_{1b} - \omega' - i\Gamma_{1b})(\omega_{12} + \omega'' + \omega''' + i\Gamma_{12})(\omega_{1d} + \omega'''' + i\Gamma_{1d})} \quad (x)$$

$$+ \frac{d_{1b}^{\alpha_1} d_{b2}^{\alpha_2} d_{2d}^u d_{d1}^{\alpha_3}}{(\omega_{1b} - \omega' - i\Gamma_{1b})(\omega_{12} - \omega' - \omega''' - i\Gamma_{12})(\omega_{1d} + \omega'''' + i\Gamma_{1d})} \quad (xi)$$

$$+ \frac{d_{1b}^{\alpha_1} d_{b2}^{\alpha_2} d_{2d}^{\alpha_3} d_{d1}^u}{(\omega_{1b} - \omega' - i\Gamma_{1b})(\omega_{12} - \omega' - \omega''' - i\Gamma_{12})(\omega_{1d} - \omega' - \omega''' - i\Gamma_{1d})} \quad (xii)$$

$$+ \rho_{22}^0 \left[\frac{d_{2b}^u d_{b1}^{\alpha_1} d_{1d}^{\alpha_2} d_{d2}^{\alpha_3}}{(\omega_{2b} + \omega' + \omega'' + \omega''' + i\Gamma_{2b})(\omega_{21} + \omega'' + \omega''' + i\Gamma_{21})(\omega_{2d} + \omega'''' + i\Gamma_{2d})} \right] \quad (xiii)$$

$$+ \frac{d_{2b}^{\alpha_1} d_{b1}^u d_{1d}^{\alpha_2} d_{d2}^{\alpha_3}}{(\omega_{2b} - \omega' - i\Gamma_{2b})(\omega_{21} + \omega'' + \omega''' + i\Gamma_{21})(\omega_{2d} + \omega'''' + i\Gamma_{2d})} \quad + \dots \quad (xiv)$$

(4.21)

In Eq (4.21), the contribution from only a single rotational state is shown for the sum. Also the nonadjacent states are to be lumped together in a nonresonant term. Depending on the temperature of the system, the state density, ρ_{aa}^0 , will be either zero or nonzero. Since the procedure to be carried out here in establishing the resonant terms and calculating the specific form of $\bar{p}^{(3)}$ is identically similar for any population distribution, only a single vibrational-rotational state will be retained with all but ρ_{00}^0 and ρ_{11}^0 ignored. The results obtained are easily generalized to include all possible vibrational-rotational levels.

The transition frequencies, ω_{ac} , thus take on the specific values ω_{10} and ω_{01} where $\omega_{01} = -\omega_{10}$. Resonant combinations that occur from Expression (4.20) are

$$\omega_{10} = \omega_1 + \omega_2 \pm i\Gamma_{10}$$

$$\omega_{01} + \omega_1 - \omega_2 \pm i\Gamma_{10}$$

$$\omega_{10} = \omega_3 + \omega_1 \pm i\Gamma_{10}$$

$$\omega_{01} + \omega_3 - \omega_1 \pm i\Gamma_{10}$$

$$\omega_{10} = \omega_2 + \omega_4 \pm i\Gamma_{10}$$

$$\omega_{01} + \omega_2 - \omega_4 \pm i\Gamma_{10} \quad (4.22)$$

where \pm indicate either + or - may occur. The field localization property serves to determine the existence of any of these sums. For example, consider the specific product from the first term on the RHS of Eq (4.9)

$$\pi_1 = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(-\omega; \omega', \omega'', \omega''') a_1^{\alpha_1} a_1^{\alpha_2} a_1^{\alpha_3} \\ \times \epsilon_1(\omega') \epsilon_1(\omega'') \epsilon_1(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.23)$$

Since $\epsilon_1(\omega)$ is only nonzero in a region about ω_1 , the polarizability can only take on the form $p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(-3\omega_1; \omega_1, \omega_1, \omega_1)$ which is easily seen for the monochromatic field of Eq (4.6i). But with this functional dependence, none of the linear combinations of Expression (4.22) will occur and this polarizability is nonresonant. A second example is the specific product from the second RHS term of Eq (4.9)

$$\pi_2 = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(-\omega; \omega', \omega'', \omega''') a_1^{*\alpha_1} a_1^{\alpha_2} a_2^{\alpha_3} \\ \times \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.24)$$

Here the polarizability becomes $p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(-\omega_2; -\omega_1, \omega_1, \omega_2)$. From Eq (4.21) terms (iii) and (iv), the linear combination $\omega_{01} + \omega - \omega - i\Gamma_{01}$ occurs as one of the six terms arising from the symmetrizing operation. Specifically, this occurs when (iii) has the index order $\alpha_1, \alpha_3, \mu, \alpha_2$ and $\alpha_3, \alpha_1, \mu, \alpha_2$ and (iv) has the index order $\alpha_1, \alpha_3, \alpha_2, \mu$ and $\alpha_3, \alpha_1, \alpha_2, \mu$. Terms (v) and (vi) of Eq (4.21) have the linear combination $\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}$ for the order $\alpha_2, \alpha_1, \alpha_3$ with index μ in the proper location. Thus, this polarizability is resonant and would be retained. This procedure has been used to create tables which summarize the central frequencies, number of similar terms, existence of resonances, and resonant term in the polarizability from Eq (4.21). Tables III and IV, are for RHS terms 1 and 2, of Eq (4.9), respectively. Tables for RHS terms 3 and 4 are not necessary since with intrinsic permutation symmetry as demonstrated in this section these terms are equivalent to RHS term 2. For example, products $\epsilon_1^{\alpha_1}(\omega')\epsilon_1^{*\alpha_2}(\omega'')\epsilon_3^{\alpha_3}(\omega''')$ and $\epsilon_3^{\alpha_1}(\omega')\epsilon_1^{\alpha_2}(\omega'')\epsilon_1^{*\alpha_3}(\omega''')$ by changing dummy variables and intrinsic permutation symmetry are equivalent to $\epsilon_1^{*\alpha_1}(\omega')\epsilon_1^{\alpha_2}(\omega'')\epsilon_3^{\alpha_3}(\omega''')$. Thus the number of similar terms in Table IV is increased by a factor of three. If the resonant terms for field components localized about $\omega_1, \omega_2, \omega_3$ and ω_4 are retained explicitly and the remainder of the terms lumped together in a single nonresonant polarizability, only sixteen resonant products remain to be considered. This can be seen from Tables III and IV.

Before writing out the field component products of interest in this work, a comment on the field component localization is necessary. It is being assumed that four field components exist as above which

TABLE III

Equation (4.9) First Term Field Products

| $\epsilon_i \epsilon_j \epsilon_k$ | Central Frequency ω' , ω'' , $\omega''' \rightarrow \omega$ | Similar Terms | Resonance | EQ (4.21) Terms |
|------------------------------------|--|---------------|-----------|--------------------|
| 1 1 1 | $\omega_1 \quad \omega_1 \quad \omega_1 \quad 3\omega_1$ | 1 | No | |
| 1 1 2 | $\omega_1 \quad \omega_1 \quad \omega_2 \quad 2\omega_1 + \omega_2$ | 3 | No | |
| 1 2 2 | $\omega_1 \quad \omega_2 \quad \omega_2 \quad 2\omega_2 + \omega_1$ | 3 | No | |
| 2 2 2 | $\omega_2 \quad \omega_2 \quad \omega_2 \quad 3\omega_2$ | 1 | No | |
| 1 1 3 | $\omega_1 \quad \omega_1 \quad \omega_3 \quad 4\omega_1 - \omega_2$ | 3 | No | |
| 1 1 4 | $\omega_1 \quad \omega_1 \quad \omega_4 \quad 2\omega_2 + \omega_1$ | 3 | No | |
| 1 2 3 | $\omega_1 \quad \omega_2 \quad \omega_3 \quad 3\omega_1$ | 6 | No | |
| 1 2 4 | $\omega_1 \quad \omega_2 \quad \omega_4 \quad 3\omega_2$ | 6 | No | |
| 1 3 3 | $\omega_1 \quad \omega_3 \quad \omega_3 \quad 5\omega_1 - 2\omega_2$ | 3 | No | |
| 1 3 4 | $\omega_1 \quad \omega_3 \quad \omega_4 \quad 2\omega_1 + \omega_2$ | 6 | No | None |
| 1 4 4 | $\omega_1 \quad \omega_4 \quad \omega_4 \quad 4\omega_2 - \omega_1$ | 3 | No | |
| 2 2 3 | $\omega_2 \quad \omega_2 \quad \omega_3 \quad 2\omega_1 + \omega_2$ | 3 | No | |
| 2 2 4 | $\omega_2 \quad \omega_2 \quad \omega_4 \quad 4\omega_2 - \omega_1$ | 3 | No | |
| 2 3 3 | $\omega_2 \quad \omega_3 \quad \omega_3 \quad 4\omega_1 - \omega_2$ | 3 | No | |
| 2 3 4 | $\omega_2 \quad \omega_3 \quad \omega_4 \quad 2\omega_2 + \omega_1$ | 6 | No | |
| 2 4 4 | $\omega_2 \quad \omega_4 \quad \omega_4 \quad 5\omega_2 - 2\omega_1$ | 3 | No | |
| 3 3 3 | $\omega_3 \quad \omega_3 \quad \omega_3 \quad 6\omega_1 - 3\omega_2$ | 1 | No | |
| 3 3 4 | $\omega_3 \quad \omega_3 \quad \omega_4 \quad 3\omega_1$ | 3 | No | |
| 3 4 4 | $\omega_3 \quad \omega_4 \quad \omega_4 \quad 3\omega_2$ | 3 | No | |
| 4 4 4 | $\omega_4 \quad \omega_4 \quad \omega_4 \quad 6\omega_2 - 3\omega_1$ | 1 | No | |

TABLE IV
Equation (4.9) Second Term Field Products

| ϵ_i^* ϵ_j ϵ_k | Central Frequency $\omega_1, \omega_2, \omega_3, \omega_4 \rightarrow \omega$ | Similar Terms | Resonance | EQ (4.21) Terms |
|--|--|---------------|-----------|--------------------|
| 1 1 1 | $-\omega_1 \quad \omega_1 \quad \omega_1 \quad \omega_1$ | 1 | No | |
| 1 1 2 | $-\omega_1 \quad \omega_1 \quad \omega_2 \quad \omega_2$ | 2 | Yes | (iii) thru (vi) |
| 1 2 2 | $-\omega_1 \quad \omega_2 \quad \omega_2 \quad 2\omega_2 - \omega_1 = \omega_4$ | 1 | Yes | (iii) thru (vi) |
| 2 1 1 | $-\omega_2 \quad \omega_1 \quad \omega_1 \quad 2\omega_1 - \omega_2 = \omega_3$ | 1 | Yes | (i)(ii)(vii)(viii) |
| 2 2 1 | $-\omega_2 \quad \omega_2 \quad \omega_1 \quad \omega_1$ | 2 | Yes | (i)(ii)(vii)(viii) |
| 2 2 2 | $-\omega_2 \quad \omega_2 \quad \omega_2 \quad \omega_2$ | 1 | No | |
| 1 1 3 | $-\omega_1 \quad \omega_1 \quad \omega_3 \quad \omega_3$ | 2 | Yes | (i)(ii)(vii)(viii) |
| 1 1 4 | $-\omega_1 \quad \omega_1 \quad \omega_4 \quad \omega_4$ | 2 | No | |
| 1 2 3 | $-\omega_1 \quad \omega_2 \quad \omega_3 \quad \omega_1$ | 2 | Yes | (i) thru (viii) |
| 1 2 4 | $-\omega_1 \quad \omega_2 \quad \omega_4 \quad 3\omega_2 - 2\omega_1$ | 2 | Yes | (iii) thru (vi) |
| 1 3 3 | $-\omega_1 \quad \omega_3 \quad \omega_3 \quad 3\omega_1 - 2\omega_2$ | 1 | Yes | (i)(ii)(vii)(viii) |
| 1 4 3 | $-\omega_1 \quad \omega_4 \quad \omega_3 \quad \omega_2$ | 2 | Yes | (i)(ii)(vii)(viii) |
| 1 4 4 | $-\omega_1 \quad \omega_4 \quad \omega_4 \quad 4\omega_2 - 3\omega_1$ | 1 | No | |
| 2 1 3 | $-\omega_2 \quad \omega_1 \quad \omega_3 \quad 3\omega_1 - 2\omega_2$ | 2 | Yes | (i)(ii)(vii)(viii) |
| 2 2 3 | $-\omega_2 \quad \omega_2 \quad \omega_3 \quad \omega_3$ | 2 | No | |
| 2 2 4 | $-\omega_2 \quad \omega_2 \quad \omega_4 \quad \omega_4$ | 2 | Yes | (iii) thru (vi) |
| 2 3 3 | $-\omega_2 \quad \omega_3 \quad \omega_3 \quad 4\omega_1 - 3\omega_2$ | 1 | No | |
| 2 3 4 | $-\omega_2 \quad \omega_3 \quad \omega_4 \quad \omega_1$ | 2 | Yes | (iii) thru (vi) |
| 2 4 1 | $-\omega_2 \quad \omega_4 \quad \omega_1 \quad \omega_2$ | 2 | Yes | (i) thru (viii) |
| 2 4 4 | $-\omega_2 \quad \omega_4 \quad \omega_4 \quad 3\omega_2 - 2\omega_1$ | 1 | Yes | (iii) thru (vi) |
| 3 1 2 | $-\omega_3 \quad \omega_1 \quad \omega_2 \quad \omega_4$ | 2 | Yes | (iii) thru (vi) |
| 3 1 4 | $-\omega_3 \quad \omega_1 \quad \omega_4 \quad 3\omega_2 - 2\omega_1$ | 2 | Yes | (iii) thru (vi) |
| 3 2 2 | $-\omega_3 \quad \omega_2 \quad \omega_2 \quad 3\omega_2 - 2\omega_1$ | 1 | No | |
| 3 2 3 | $-\omega_3 \quad \omega_2 \quad \omega_3 \quad \omega_2$ | 2 | No | |
| 3 2 4 | $-\omega_3 \quad \omega_2 \quad \omega_4 \quad 4\omega_2 - 3\omega_1$ | 2 | No | |
| 3 3 1 | $-\omega_3 \quad \omega_3 \quad \omega_1 \quad \omega_1$ | 2 | Yes | (iii) thru (vi) |
| 3 3 3 | $-\omega_3 \quad \omega_3 \quad \omega_3 \quad \omega_3$ | 1 | No | |
| 3 3 4 | $-\omega_3 \quad \omega_3 \quad \omega_4 \quad \omega_4$ | 2 | No | |
| 3 4 4 | $-\omega_3 \quad \omega_4 \quad \omega_4 \quad 5\omega_2 - 4\omega_1$ | 1 | No | |
| 3 1 1 | $-\omega_3 \quad \omega_1 \quad \omega_1 \quad \omega_2$ | 1 | Yes | (iii) thru (vi) |
| 4 1 1 | $-\omega_4 \quad \omega_1 \quad \omega_1 \quad 3\omega_1 - 2\omega_2$ | 1 | No | |
| 4 1 2 | $-\omega_4 \quad \omega_1 \quad \omega_2 \quad \omega_3$ | 2 | Yes | (i)(ii)(vii)(viii) |
| 4 1 3 | $-\omega_4 \quad \omega_1 \quad \omega_3 \quad 4\omega_1 - 3\omega_2$ | 2 | No | |
| 4 1 4 | $-\omega_4 \quad \omega_1 \quad \omega_4 \quad \omega_1$ | 2 | No | |
| 4 2 2 | $-\omega_4 \quad \omega_2 \quad \omega_2 \quad \omega_1$ | 1 | Yes | (i)(ii)(vii)(viii) |
| 4 2 3 | $-\omega_4 \quad \omega_2 \quad \omega_3 \quad 3\omega_1 - 2\omega_2$ | 2 | Yes | (i)(ii)(vii)(viii) |
| 4 3 3 | $-\omega_4 \quad \omega_3 \quad \omega_3 \quad 5\omega_1 - 4\omega_2$ | 1 | No | |
| 4 3 4 | $-\omega_4 \quad \omega_3 \quad \omega_4 \quad \omega_3$ | 2 | No | |
| 4 4 2 | $-\omega_4 \quad \omega_4 \quad \omega_2 \quad \omega_2$ | 2 | Yes | (i)(ii)(vii)(viii) |
| 4 4 4 | $-\omega_4 \quad \omega_4 \quad \omega_4 \quad \omega_4$ | 1 | No | |

may or may not be monochromatic. These components, actually the amplitude distribution function of the field in frequency space, are assumed to be localized in a finite band of frequency domain roughly centered about the frequencies ω_1 , ω_2 , ω_3 and ω_4 . These bands are assumed to be sufficiently separated such that there is no overlap (i.e., at any given frequency, only one component of the field exists and all other components are zero at that frequency). Figure 3 depicts the situation described. Since the input fields, $\bar{E}_1(\omega)$ and $\bar{E}_2(\omega)$, are controllable, from Figure 3 the condition that they not overlap

$$\delta_2 + \delta_1' < \omega_v \quad (4.25)$$

can be assured. It should be noted, however, that although the frequency bands of $\bar{E}_1(\omega)$ and $\bar{E}_2(\omega)$ do not overlap the effect of frequency mixing to get ω_3 and ω_4 can increase the frequency bandwidth and cause an overlap between adjacent fields. For the case of low conversion efficiency in generating \bar{E}_3 and \bar{E}_4 (and higher order fields) by the nonlinear polarization, these fields in any overlap region would be extremely weak (i.e., the off resonance effect of $\bar{p}^{(3)}$ in the frequency wings decreases the polarization and hence \bar{E}_3 and \bar{E}_4 there). Within the bandwidth of the input fields, the generated fields may then be neglected with little or no impact on measurable signals. However, for the case of high conversion efficiency, where the input fields are significantly depleted the generated fields may be of a comparable value (depending upon the off-resonance effect of the polarizability, the frequency bandwidth involved, etc.). The total field in a given frequency domain may then consist of more than

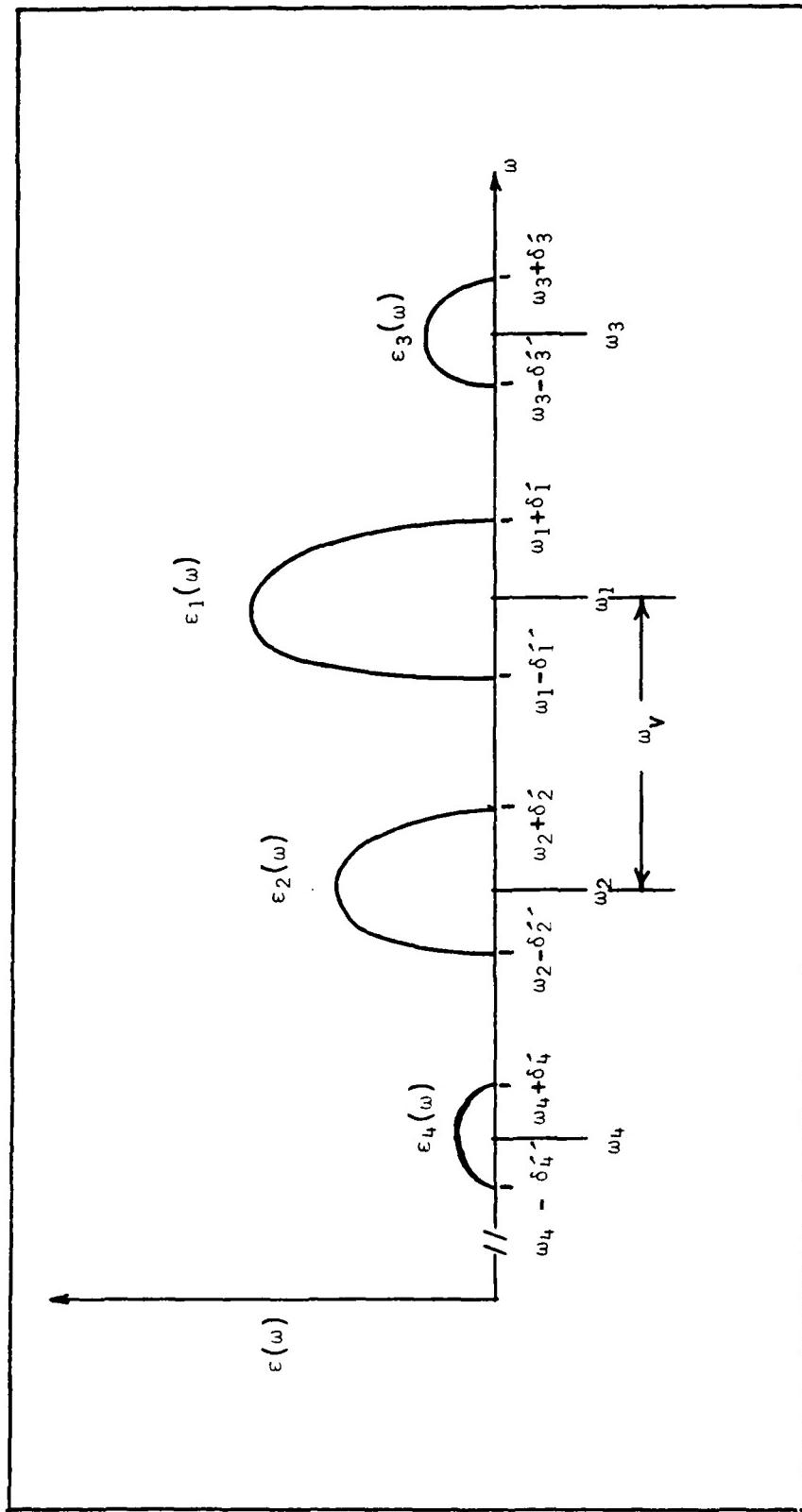


Figure 3. Field Amplitude Distribution Functions
In Frequency Space

one field (e.g., $\epsilon_1(\omega)$ and $\epsilon_3(\omega)$ are nonzero at a frequency $\omega_1 + \delta_1$).

The separation of the frequency dependent equations into independent equations using the principle of superposition is not allowed.

A criterion on the finite bandwidth of the fields is then necessary to allow the separation of the field equations. At resonance, Eq (4.2) holds and defines the relationship between the central frequencies ω_1 and ω_2 . Using the definitions of ω_3 and ω_4 with the resonance condition, Eq (4.2)

$$\begin{aligned}\omega_3 &= 2\omega_1 - \omega_2 = \omega_1 + \omega_v \\ \omega_4 &= 2\omega_2 - \omega_1 = \omega_2 - \omega_v\end{aligned}\tag{4.26}$$

or in general, the frequencies generated by the Raman resonances may be written as

$$\begin{aligned}\omega_n &= \omega_1 + \left(\frac{n-1}{2}\right) \omega_v \quad n=1,3,5,\dots \\ \omega_n &= \omega_2 - \left(\frac{n-2}{2}\right) \omega_v \quad n=2,4,6,\dots\end{aligned}\tag{4.27}$$

so that the separation of central frequencies in Figure 3 is as depicted. The effect of these linear combinations of frequency results in the bandwidth limits of each central frequency being defined in terms of the input frequency limits, $\delta_1, \delta_1', \delta_2$ and δ_2' as defined in Figure 3. These are

$$\begin{aligned}\delta_3 &= 2\delta_1 + \delta_2' \\ \delta_3' &= 2\delta_1' + \delta_2\end{aligned}\tag{4.28}$$

$$\begin{aligned}\delta_4 &= 2\delta_2 + \delta_1 \\ \delta_4' &= 2\delta_2' + \delta_1'\end{aligned}\quad (4.29)$$

In general

$$\begin{aligned}\delta_n' &= \left(\frac{n+1}{2}\right) \delta_1 + \left(\frac{n-1}{2}\right) \delta_2' \\ n &= 1, 3, 5, \dots\end{aligned}$$

$$\delta_n'' = \left(\frac{n+1}{2}\right) \delta_1' + \left(\frac{n-1}{2}\right) \delta_2 \quad (4.30)$$

$$\begin{aligned}\delta_n' &= \left(\frac{n}{2}\right) \delta_2 + \left(\frac{n-2}{2}\right) \delta_1 \\ n &= 2, 4, 6, \dots\end{aligned}$$

$$\delta_n'' = \left(\frac{n}{2}\right) \delta_2' + \left(\frac{n-2}{2}\right) \delta_1 \quad (4.31)$$

Two adjacent widths can then be expressed as

$$\delta_n'' + \delta_{n+2}' = \frac{n}{2} \left[(\delta_1 + \delta_1') + (\delta_2 + \delta_2') \right] + \delta_2 - \delta_1 \quad n \geq 2 \quad (n \text{ even})$$

$$\delta_n' + \delta_{n+2}'' = \frac{n+1}{2} \left[(\delta_1 + \delta_1') + (\delta_2 + \delta_2') \right] + \delta_1' - \delta_2' \quad n \geq 1 \quad (n \text{ odd}) \quad (4.32)$$

As an example, to see the restrictions on the E_1 and E_2 widths, $(\delta_1 + \delta_1')$ and $(\delta_2 + \delta_2')$ respectively, take the central frequency to be centered and the total widths to be approximately equal. With these approximations, Eq (4.32) then yields

$$\begin{aligned} n(\delta' + \delta'') &< \omega_v & n &\geq 2 \text{ (n even)} \\ (n+1)(\delta' + \delta'') &< \omega_v & n &\geq 1 \text{ (n odd)} \end{aligned} \quad (4.33)$$

and

$$\begin{aligned} (\delta' + \delta'') &< \frac{\omega_v}{n} & n &\geq 2 \text{ (n even)} \\ (\delta' + \delta'') &< \frac{\omega_v}{n+1} & n &\geq 1 \text{ (n odd)} \end{aligned} \quad (4.34)$$

Therefore, if higher order field terms become important and overlap is to be eliminated, the restriction on the widths of E_1 and E_2 becomes more severe. Note that δ' and δ'' were defined as the frequency at which the field amplitude became zero. Any other consistent definition based on the field component amplitude would also work.

A lower limit for the multifrequency bandwidth is determined by the experiment in those experimental situations when dealing with the Q-branch, the vibrational-rotational energy spacing of allowed transitions typically decreases as higher values of J are considered so that if

$$\omega_{10}(0) = \frac{\Delta E (J' = 0)}{\hbar} \quad (4.35)$$

then

$$\omega_{10}(0) = \omega_{10}(1) + \Delta' \omega = \omega_{10}(2) + \Delta' \omega + \Delta'' \omega \quad (4.36)$$

where $\Delta' \omega$, $\Delta'' \omega$, etc., are quite small. Typically the magnitude of the rotational energy level spacing, ω_J , is

$$\omega_J \sim 0 (10^{-3} \omega_v) \quad (4.37)$$

The decrease in Q-branch energy level spacing is approximately

$$\Delta' \omega \sim 0 (10^{-1} - 10^{-2} \omega_J) \sim 0 (10^{-4} - 10^{-5} \omega_V) \quad (4.38)$$

Then if the pump field is monochromatic, $\delta'_1 + \delta''_1 \sim 0$. For a Stokes field width such that

$$\delta'_2 + \delta''_2 \sim 0 (10^{-2} \omega_V) \quad (4.39)$$

the entire Q-branch should be observable (Ref 82). Hydrogen with its large energy spacing is an exception and only a few of the Q-branch lines would be observed. For input bandwidths of this magnitude, very high order fields ($n \sim 100$) must be considered before overlap of the field components would occur. Thus the approximation of no field component overlap in frequency is good for a carefully defined multifrequency CARS experiment.

Equation (4.9) can now be written using the results obtained in this section to include sixteen resonant terms and a single nonresonant term

$$\langle \bar{d}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''')] : \hat{a}_2^* \hat{a}_2 \hat{a}_1 \\ \epsilon_2^*(-\omega') \epsilon_2(\omega'') \epsilon_1(\omega''')] \quad (ii)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_2 \hat{a}_3 \epsilon_1^*(-\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \quad (iii)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_3 \hat{a}_1 \epsilon_3^*(-\omega') \epsilon_3(\omega'') \epsilon_1(\omega''') \quad (iv)$$

$$+ 3\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_4^* \hat{a}_2 \hat{a}_2 \epsilon_4^*(-\omega') \epsilon_2(\omega'') \epsilon_2(\omega''') \quad (v)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_3 \hat{a}_4 \epsilon_2^*(-\omega') \epsilon_3(\omega'') \epsilon_4(\omega''') \quad (vi)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_1 \hat{a}_2 \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \quad (vii)$$

$$+ 3\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_1 \hat{a}_1 \epsilon_3^*(-\omega') \epsilon_1(\omega'') \epsilon_1(\omega''') \quad (viii)$$

$$+6\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_2^* \hat{a}_4 \hat{a}_1 \epsilon_2^*(-\omega^-) \epsilon_4(\omega^{\prime -}) \epsilon_1(\omega^{\prime \prime -}) \quad (\text{viii})$$

$$+6\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_1^* \hat{a}_4 \hat{a}_3 \epsilon_1^*(-\omega^-) \epsilon_4(\omega^{\prime -}) \epsilon_3(\omega^{\prime \prime -}) \quad (\text{ix})$$

$$+6\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_4^* \hat{a}_4 \hat{a}_2 \epsilon_4^*(-\omega^-) \epsilon_4(\omega^{\prime -}) \epsilon_2(\omega^{\prime \prime -}) \quad (\text{x})$$

$$+3\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_2^* \hat{a}_1 \hat{a}_1 \epsilon_2^*(-\omega^-) \epsilon_1(\omega^{\prime -}) \epsilon_1(\omega^{\prime \prime -}) \quad (\text{xi})$$

$$+6\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_1^* \hat{a}_1 \hat{a}_3 \epsilon_1^*(-\omega^-) \epsilon_1(\omega^{\prime -}) \epsilon_3(\omega^{\prime \prime -}) \quad (\text{xii})$$

$$+6\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_4^* \hat{a}_1 \hat{a}_2 \epsilon_4^*(-\omega^-) \epsilon_1(\omega^{\prime -}) \epsilon_2(\omega^{\prime \prime -}) \quad (\text{xiii})$$

$$+3\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_1^* \hat{a}_2 \hat{a}_2 \epsilon_1^*(-\omega^-) \epsilon_2(\omega^{\prime -}) \epsilon_2(\omega^{\prime \prime -}) \quad (\text{xiv})$$

$$+6\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_3^* \hat{a}_1 \hat{a}_2 \epsilon_3^*(-\omega^-) \epsilon_1(\omega^{\prime -}) \epsilon_2(\omega^{\prime \prime -}) \quad (\text{xv})$$

$$+6\bar{p}^{(3)}(-\omega; \omega^-, \omega^{\prime -}, \omega^{\prime \prime -}) : \hat{a}_2^* \hat{a}_2 \hat{a}_4 \epsilon_2^*(-\omega^-) \epsilon_2(\omega^{\prime -}) \epsilon_4(\omega^{\prime \prime -}) \quad (\text{xvi})$$

$$+N.R. + C.C.] \delta(\omega - \omega^- - \omega^{\prime -} - \omega^{\prime \prime -}) \quad (4.40)$$

In Eq (4.40) the field component products have been ordered first with respect to the central frequency of the dipole moment, ω , and then in decreasing magnitude of the product within the frequency grouping. Each of the terms in Eq (4.40) represents a specific process at the central frequency ω . For example, term (xi) describes the CARS process at the central frequency ω_3 . Each of the terms in Eq (4.40) and the process related to it will be discussed later in this section.

Because of the localization of the field components and the integration over this field function, the dipole moment is a linear superposition and may be divided into four separate moment equations in distinct regions of frequency space. Equation (4.40) then becomes

For $\omega_1 - \delta_1^- \leq \omega \leq \omega_1 + \delta_1^+$

$$\begin{aligned} \langle \bar{d}^{(3)}(\omega) \rangle &= \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''')] : \hat{a}_2^* \hat{a}_2 \hat{a}_1 \\ &\quad \epsilon_2^*(-\omega') \epsilon_2(\omega'') \epsilon_1(\omega''') \quad (i) \\ &+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_2 \hat{a}_3 \epsilon_1^*(-\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \quad (ii) \\ &+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_3 \hat{a}_1 \epsilon_3^*(-\omega') \epsilon_3(\omega'') \epsilon_1(\omega''') \quad (iii) \\ &+ 3\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_4^* \hat{a}_2 \hat{a}_2 \epsilon_4^*(-\omega') \epsilon_2(\omega'') \epsilon_2(\omega''') \quad (iv) \\ &+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_3 \hat{a}_4 \epsilon_2^*(-\omega') \epsilon_3(\omega'') \epsilon_4(\omega''') \quad (v) \\ &+ N.R.] \times \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (4.41)$$

For $\omega_2 - \delta_2^- \leq \omega \leq \omega_2 + \delta_2^+$

$$\begin{aligned} \langle \bar{d}^{(3)}(\omega) \rangle &= \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''')] : \hat{a}_1^* \hat{a}_1 \hat{a}_2 \\ &\quad \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \quad (i) \\ &+ 3\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_1 \hat{a}_1 \epsilon_3^*(-\omega') \epsilon_1(\omega'') \epsilon_1(\omega''') \quad (ii) \\ &+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_4 \hat{a}_1 \epsilon_2^*(-\omega') \epsilon_4(\omega'') \epsilon_1(\omega''') \quad (iii) \\ &+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_4 \hat{a}_3 \epsilon_1^*(-\omega') \epsilon_4(\omega'') \epsilon_3(\omega''') \quad (iv) \\ &+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_4^* \hat{a}_4 \hat{a}_2 \epsilon_4^*(-\omega') \epsilon_4(\omega'') \epsilon_2(\omega''') \quad (v) \\ &+ N.R.] \times \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (4.42)$$

For $\omega_3 - \delta_3^- \leq \omega \leq \omega_3 + \delta_3^+$

$$\langle \bar{d}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [3\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''')] : \hat{a}_2^* \hat{a}_1 \hat{a}_1 \\ \epsilon_2^*(-\omega') \epsilon_1(\omega'') \epsilon_1(\omega''')] \quad (i)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_1 \hat{a}_3 \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_3(\omega''') \quad (ii)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_4^* \hat{a}_1 \hat{a}_2 \epsilon_4^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \quad (iii)$$

$$+ N.R.] \times \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.43)$$

For $\omega_4 - \delta_4^- \leq \omega \leq \omega_4 + \delta_4^+$

$$\langle \bar{d}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [3\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''')] : \hat{a}_1^* \hat{a}_2 \hat{a}_2 \\ \epsilon_1^*(-\omega') \epsilon_2(\omega'') \epsilon_2(\omega''')] \quad (i)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_1 \hat{a}_2 \epsilon_3^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \quad (ii)$$

$$+ 6\bar{p}^{(3)}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_2 \hat{a}_4 \epsilon_2^*(-\omega') \epsilon_2(\omega'') \epsilon_4(\omega''') \quad (iii)$$

$$+ N.R.] \times \delta(\omega - \omega' - \omega'' - \omega''') \quad (4.44)$$

The terms in Eqs (4.41) through (4.44) represent the resonant third order processes for the four fields being considered. For consistency, the process starts with the molecule in a ground state. When there is any possibility of confusion, the process name is labeled by the resultant central frequency of the mixing (e.g., for the resultant frequency ω_1 ; CARS (1)). The inverse process is not presented since the density matrix elements of $\bar{p}^{(3)}$ automatically includes the inverse. The six processes described by Eqs (4.41) through (4.44) can be divided into two classes; parametric and

non-parametric (Ref 81:4). In a parametric process, the molecule is left, after scattering, in the initial state. In nonparametric processes, the molecule, after scattering, is left in a final state different from the initial. Nonparametric processes do not require consideration of phase matching of the wave vectors. Table V lists the processes considered here in their respective classes. To aid in identifying and understanding these processes, energy level diagrams similar to the one in Figure 2 are given along with the Feynman diagram for the resonant term only.

TABLE V
Third Order Processes - Four Fields

Nonparametric

Stimulated Raman Scattering - Stokes (SRS-S)

Stimulated Raman Scattering - Pump (SRS-P)
(IRS in Table I)

Stimulated Raman Scattering - Second Stokes (SRS-SS)

Parametric

Coherent Anti-Stokes Raman Scattering (CARS)

Coherent Stokes Raman Scattering (CSRS)

Coherent Mixed Raman Scattering (CMRS)

The diagrams for the nonparametric and parametric processes are given in Figures 4 and 5, respectively. The appropriate field component products for each process are included. These scattering processes

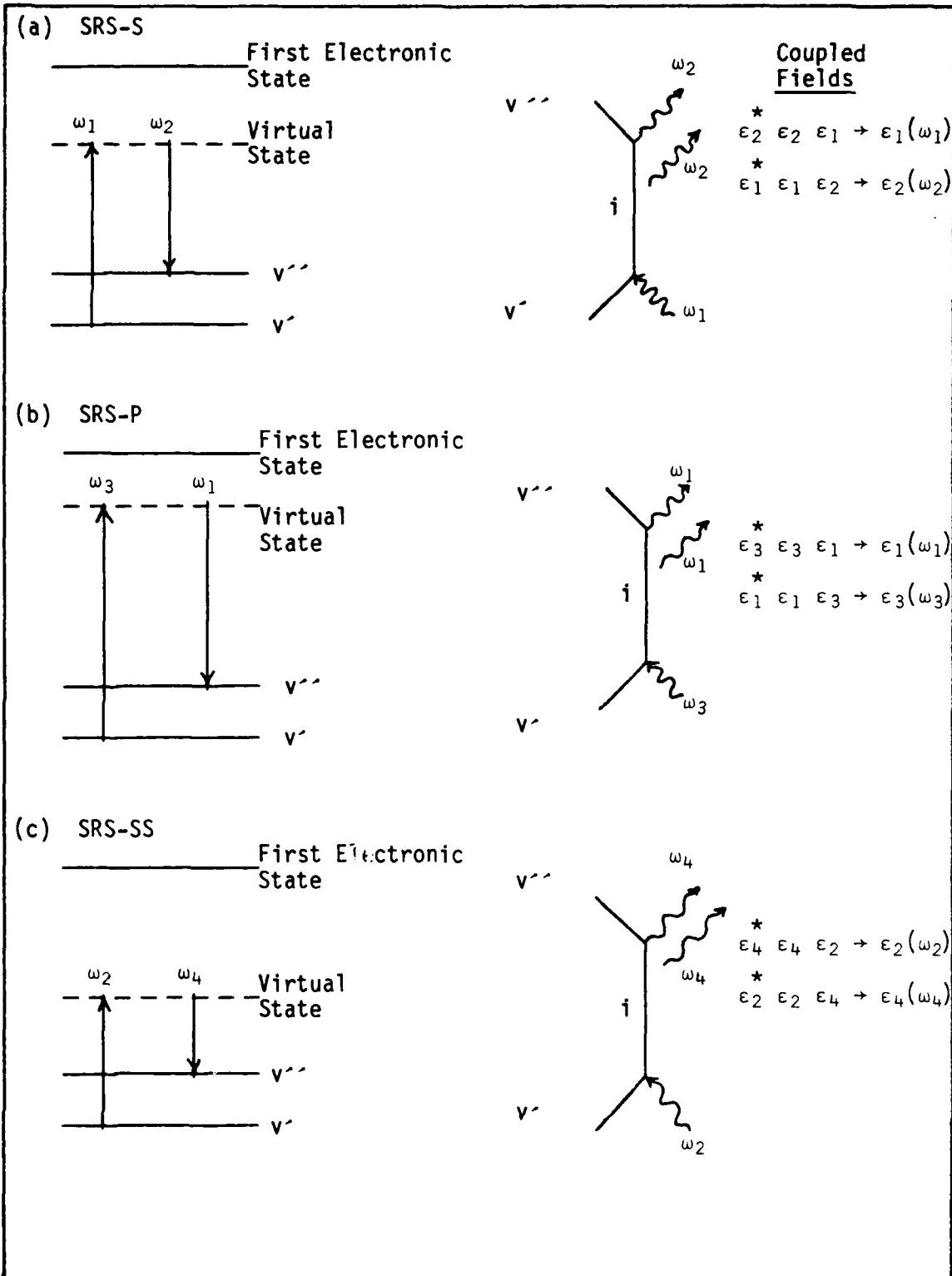


Figure 4. Diagrams for Nonparametric Third Order Scattering Processes with Four Fields

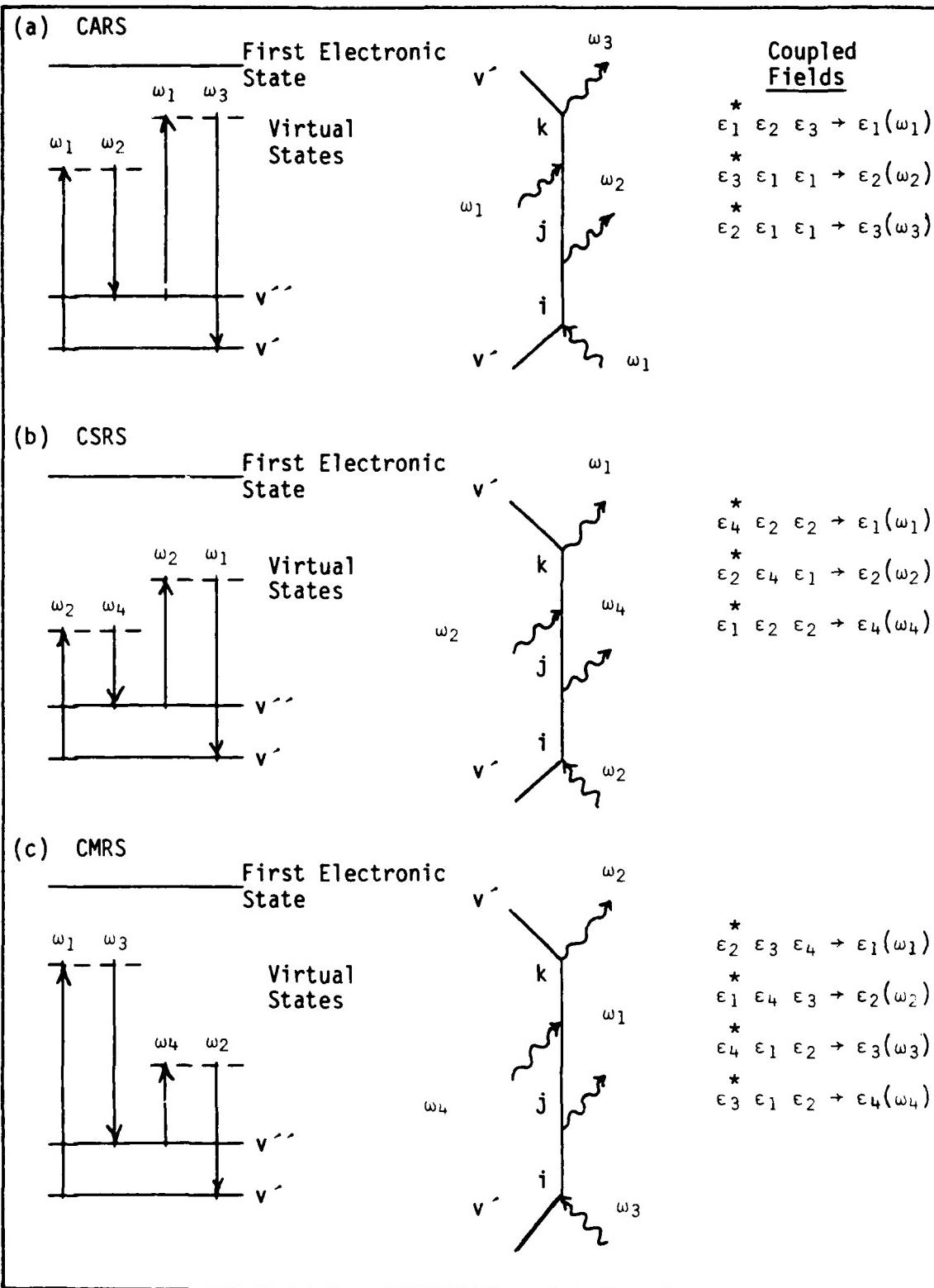


Figure 5. Diagrams for Parametric Third Order Scattering Processes with Four Fields

represent the complete set of third order resonant terms for two input fields plus the largest two generated fields. Equations (4.41) through (4.44) are rewritten with the polarizability term identified by the scattering process

$$\begin{aligned}
 & (i) \omega_1 - \delta_1' \leq \omega \leq \omega_1 + \delta_1' \\
 & \langle \bar{d}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [6\bar{p}^{SRS-S}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_2 \hat{a}_1 \\
 & \quad \epsilon_2^*(-\omega') \epsilon_2(\omega'') \epsilon_1(\omega''')] \\
 & \quad + 6\bar{p}^{CARS}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_2 \hat{a}_3 \epsilon_1^*(-\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \\
 & \quad + 6\bar{p}^{SRS-P}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_3 \hat{a}_1 \epsilon_3^*(-\omega') \epsilon_3(\omega'') \epsilon_1(\omega''') \\
 & \quad + 3\bar{p}^{CSRS}(-\omega; \omega', \omega'', \omega''') : \hat{a}_4^* \hat{a}_2 \hat{a}_2 \epsilon_4^*(-\omega') \epsilon_2(\omega'') \epsilon_2(\omega''') \\
 & \quad + 6\bar{p}^{CMRS}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_3 \hat{a}_4 \epsilon_2^*(-\omega') \epsilon_3(\omega'') \epsilon_4(\omega''') \\
 & \quad + N.R.] \delta(\omega - \omega' - \omega'' - \omega''') \tag{4.45}
 \end{aligned}$$

$$(ii) \omega_2 - \delta_2' \leq \omega \leq \omega_2 + \delta_2'$$

$$\begin{aligned}
 & \langle \bar{d}^{(3)}(\omega) \rangle = \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [6\bar{p}^{SRS-S}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_1 \hat{a}_2 \\
 & \quad \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''')] \\
 & \quad + 3\bar{p}^{CARS}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_1 \hat{a}_1 \epsilon_3^*(-\omega') \epsilon_1(\omega'') \epsilon_1(\omega''') \\
 & \quad + 6\bar{p}^{CSRS}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_4 \hat{a}_1 \epsilon_2^*(-\omega') \epsilon_4(\omega'') \epsilon_1(\omega''') \\
 & \quad + 6\bar{p}^{CMRS}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_4 \hat{a}_3 \epsilon_1^*(-\omega') \epsilon_4(\omega'') \epsilon_3(\omega''') \\
 & \quad + 6\bar{p}^{SRS-SS}(-\omega; \omega', \omega'', \omega''') : \hat{a}_4^* \hat{a}_4 \hat{a}_2 \epsilon_4^*(-\omega') \epsilon_4(\omega'') \epsilon_2(\omega''') \\
 & \quad + N.R.] \delta(\omega - \omega' - \omega'' - \omega''') \tag{4.46}
 \end{aligned}$$

$$(iii) \omega_3 - \delta\hat{\beta} \leq \omega \leq \omega_3 + \delta\hat{\beta}$$

$$\begin{aligned} \langle \bar{d}^{(3)}(\omega) \rangle &= \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [3\bar{p}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''')] : \hat{a}_2^* \hat{a}_1 \hat{a}_1 \\ &\quad \epsilon_2^*(-\omega') \epsilon_1(\omega'') \epsilon_1(\omega''') \\ &+ 6\bar{p}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') : \hat{a}_1^* \hat{a}_1 \hat{a}_3 \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_3(\omega''') \\ &+ 6\bar{p}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') : \hat{a}_4^* \hat{a}_1 \hat{a}_2 \epsilon_4^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \\ &+ \text{N.R.}] \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (4.47)$$

$$(iv) \omega_4 - \delta\hat{\beta} \leq \omega \leq \omega_4 + \delta\hat{\beta}$$

$$\begin{aligned} \langle \bar{d}^{(3)}(\omega) \rangle &= \int_{-\infty}^{\infty} d\omega' \int_{-\infty}^{\infty} d\omega'' \int_{-\infty}^{\infty} d\omega''' [3\bar{p}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''')] : \hat{a}_1^* \hat{a}_2 \hat{a}_2 \\ &\quad \epsilon_1^*(-\omega') \epsilon_2(\omega'') \epsilon_2(\omega''') \\ &+ 6\bar{p}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') : \hat{a}_3^* \hat{a}_1 \hat{a}_2 \epsilon_3^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \\ &+ 6\bar{p}^{\text{SRS-SS}}(-\omega; \omega', \omega'', \omega''') : \hat{a}_2^* \hat{a}_2 \hat{a}_4 \epsilon_2^*(-\omega') \epsilon_2(\omega'') \epsilon_4(\omega''') \\ &+ \text{N.R.}] \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (4.48)$$

The relative magnitude of the generated fields are dependent on the input fields and the susceptibility. To obtain the resonant susceptibility, the resonant polarizability, Eq (3.22), is required.

Polarizability

The individual resonant polarizabilities of Eqs (4.45) through (4.48) can be derived from Eq (4.21) using the information in Table IV. As an example, for $\bar{p}^{\text{SRS-S}}$ of Eq (4.45), the field component product is $\epsilon_2^*(-\omega') \epsilon_2(\omega'') \epsilon_1(\omega''')$ and Table IV gives terms (i), (ii),

(vii) and (viii) of Eq (4.21) that are resonant. However, because of the symmetrization operator in Eq (4.21), there are six possible permutations for each of these terms. The specific order of indices with their corresponding frequencies determines which of the six possible permutations produce a resonance. In this example, $\alpha_1\omega'$, $\alpha_2\omega''$, $\alpha_3\omega'''$, corresponds by localization to $-\omega_2$, ω_2 , ω_1 , respectively. Thus, the resonant terms are:

Term (i); $\mu\alpha_2\alpha_1\alpha_3$ and $\mu\alpha_2\alpha_3\alpha_1$

Term (ii); $\alpha_2\mu\alpha_1\alpha_3$ and $\alpha_2\mu\alpha_3\alpha_1$

Term (vii); $\alpha_1\alpha_3\mu\alpha_2$ and $\alpha_3\alpha_1\mu\alpha_2$

Term (viii); $\alpha_1\alpha_3\alpha_2\mu$ and $\alpha_3\alpha_1\alpha_2\mu$

and Eq (4.21) after dropping the line widths for terms far from resonance becomes

$$\begin{aligned}
 & p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S (1)}} (-\omega; \omega', \omega'', \omega''') = -\frac{1}{6\hbar^3} \sum_{b,d} \rho_{00}^0 \\
 & \times \left[\frac{d_{ob}^\mu d_{b1}^{\alpha_2} d_{1d}^{\alpha_3} d_{do}^{\alpha_1}}{(\omega_{ob} + \omega' + \omega'' + \omega'') (\omega_{01} + \omega'' + \omega' + i\Gamma_{01}) (\omega_{od} + \omega')} \right. \\
 & + \frac{d_{ob}^\mu d_{b1}^{\alpha_2} d_{1d}^{\alpha_1} d_{do}^{\alpha_3}}{(\omega_{ob} + \omega'' + \omega' + \omega'') (\omega_{01} + \omega' + \omega''' + i\Gamma_{01}) (\omega_{od} + \omega''')} \\
 & + \frac{d_{ob}^{\alpha_2} d_{b1}^\mu d_{1d}^{\alpha_3} d_{do}^{\alpha_1}}{(\omega_{ob} - \omega'') (\omega_{01} + \omega'' + \omega' + i\Gamma_{01}) (\omega_{od} + \omega')} \\
 & + \left. \frac{d_{ob}^{\alpha_2} d_{b1}^\mu d_{1d}^{\alpha_1} d_{do}^{\alpha_3}}{(\omega_{ob} - \omega'') (\omega_{01} + \omega' + \omega'' + i\Gamma_{01}) (\omega_{od} + \omega'')} + \text{N.R.} \right]
 \end{aligned}$$

$$\begin{aligned}
& + \sum_{bd} p_{11}^o \left[\frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3} d_{od}^{\mu} d_{dl}^{\alpha_2}}{(\omega_{1b} - \omega') (\omega_{10} - \omega' - \omega''' - i\Gamma_{10}) (\omega_{1d} + \omega''')} \right. \\
& + \frac{d_{ob}^{\alpha_3} d_{b1}^{\alpha_1} d_{ld}^{\mu} d_{do}^{\alpha_2}}{(\omega_{1b} - \omega''') (\omega_{10} - \omega''' - \omega' - i\Gamma_{10}) (\omega_{1d} + \omega'')} \\
& + \frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3} d_{od}^{\alpha_2} d_{dl}^{\mu}}{(\omega_{1b} - \omega') (\omega_{10} - \omega' - \omega''' - i\Gamma_{10}) (\omega_{1d} - \omega' - \omega''' - \omega''')} \\
& \left. + \frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1} d_{od}^{\alpha_2} d_{dl}^{\mu}}{(\omega_{1b} - \omega''') (\omega_{10} - \omega''' - \omega' - i\Gamma_{10}) (\omega_{1d} - \omega' - \omega''' - \omega''')} + N.R. \right] \quad (4.49)
\end{aligned}$$

Since the middle denominator term in each case does not depend on b or d, it may be removed from the summation. It can also be noted that

$$\omega_{01} + \omega' + \omega''' + i\Gamma_{01} = -(\omega_{10} - \omega' - \omega''' - i\Gamma_{10}) \quad (4.50)$$

Then the first RHS term in brackets factors equal to

$$\left[\frac{d_{ob}^{\mu} d_{b1}^{\alpha_2}}{(\omega_{ob} + \omega' + \omega''' + \omega''')} + \frac{d_{ob}^{\alpha_2} d_{b1}^{\mu}}{(\omega_{ob} - \omega')} \right] \left[\frac{d_{1d}^{\alpha_1} d_{do}^{\alpha_3}}{(\omega_{od} + \omega''')} + \frac{d_{1d}^{\alpha_3} d_{do}^{\alpha_1}}{(\omega_{od} + \omega')} \right] \quad (4.51)$$

and the second bracketed term factors to

$$\left[\frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3}}{(\omega_{1b} - \omega')} + \frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1}}{(\omega_{1b} - \omega''')} \right] \left[\frac{d_{od}^{\mu} d_{dl}^{\alpha_2}}{(\omega_{1d} + \omega'')} + \frac{d_{od}^{\alpha_2} d_{dl}^{\mu}}{(\omega_{1d} - \omega' - \omega''' - \omega''')} \right] \quad (4.52)$$

Note that the first sums in Expressions (4.51) and (4.52) depend on the index b while the second sums depend on d. Equation (4.49) for $p_{\mu\alpha_1\alpha_2\alpha_3}$ now becomes

$$\begin{aligned}
& \text{SRS-S(1)} \quad p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \frac{1}{(\omega_{10} - \omega' - \omega''' - i\Gamma_{10})} \left\{ \rho_{00}^o \right. \\
& \times \sum_b \left[\frac{d_{ob}^\mu d_{bl}^{\alpha_2}}{(\omega_{ob} + \omega' + \omega'' + \omega''')} + \frac{d_{ob}^{\alpha_2} d_{bl}^\mu}{(\omega_{ob} - \omega')} \right] \times \sum_d \left[\frac{d_{1d}^{\alpha_1} d_{do}^{\alpha_3}}{(\omega_{od} + \omega''')} + \frac{d_{1d}^{\alpha_3} d_{do}^{\alpha_1}}{(\omega_{od} + \omega')} \right] \\
& - \rho \sum_b \left[\frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3}}{(\omega_{1b} - \omega')} + \frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1}}{(\omega_{1b} - \omega''')} \right] \times \sum_d \left[\frac{d_{od}^\mu d_{d1}^{\alpha_2}}{(\omega_{1d} + \omega'')} + \frac{d_{od}^{\alpha_2} d_{d1}^\mu}{(\omega_{1d} - \omega' - \omega'' - \omega''')} \right] \left. \right\} \\
& + \text{N.R.} \tag{4.53}
\end{aligned}$$

Two further simplifying changes are possible $\omega_{ij} = -\omega_{ji}$ and the dummy index d may be changed to $a b$ so that Eq (4.53) becomes

$$\begin{aligned}
& \text{SRS-S(1)} \quad p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \frac{1}{\omega_{10} - \omega' - \omega''' - i\Gamma_{10}} \\
& \times \left\{ \rho_{00}^o \sum_b \left[\frac{d_{ob}^\mu d_{bl}^{\alpha_2}}{(\omega_{bo} - \omega' - \omega''' - \omega''')} + \frac{d_{1b}^{\alpha_2} d_{bo}^\mu}{(\omega_{bo} + \omega'')} \right] \right. \\
& \times \sum_b \left[\frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3}}{(\omega_{bo} - \omega''')} + \frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1}}{(\omega_{bo} - \omega')} \right] \\
& - \rho_{11}^o \sum_b \left[\frac{d_{ob}^{\alpha_2} d_{bl}^\mu}{(\omega_{bl} + \omega' + \omega'' + \omega''')} + \frac{d_{ob}^\mu d_{bl}^{\alpha_2}}{(\omega_{bl} - \omega'')} \right] \\
& \left. \times \sum_b \left[\frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1}}{(\omega_{bl} + \omega''')} + \frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3}}{(\omega_{bl} + \omega')} \right] \right\} + \text{N.R.} \tag{4.54}
\end{aligned}$$

Equation (4.54) can be put in a more self consistent form by writing the second sum in each product as a complex conjugate. The details for this change are given in Appendix E, Eq (E30).

$$SRS-S(1) \rho_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \frac{1}{\omega_{l0} - \omega' - \omega''' - i\Gamma_{l0}}$$

$$\times \left\{ \rho_{00}^o \sum_b \left[\frac{d_{ob}^\mu d_{b1}^{\alpha_2}}{(\omega_{bo} - \omega' - \omega'' - \omega''')} + \frac{d_{ob}^{\alpha_2} d_{b1}^\mu}{(\omega_{bo} + \omega'')} \right] \right.$$

$$\left. \times \sum_b \left[\frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_3}}{(\omega_{bo} - \omega')} + \frac{d_{ob}^{\alpha_3} d_{b1}^{\alpha_1}}{(\omega_{bo} - \omega''')} \right]^* \right]$$

$$-\rho_{11}^o \sum_b \left[\frac{d_{ob}^{\alpha_2} d_{b1}^\mu}{(\omega_{b1} + \omega' + \omega'' + \omega''')} + \frac{d_{ob}^\mu d_{b1}^{\alpha_2}}{(\omega_{b1} - \omega''')} \right]$$

$$\left. \times \sum_b \left[\frac{d_{ob}^{\alpha_3} d_{b1}^{\alpha_1}}{(\omega_{b1} + \omega')} + \frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_3}}{(\omega_{b1} + \omega''')} \right]^* \right\} + N.R. \quad (4.55)$$

Equation (4.55) can be simplified in form by defining a shorthand notation:

$$\Sigma \left[\frac{d_{ob}^{\mu} d_{bl}^{\alpha_2}}{\omega_{bo} - \omega' - \omega'' - \omega''' + \omega} + \frac{d_{ob}^{\alpha_2} d_{bl}^{\mu}}{\omega_{bo} + \omega''} \right] = f_{-\omega, \omega''}^{\mu \alpha_2} \quad (i)$$

$$\Sigma \left[\frac{d_{ob}^{\alpha_1} d_{bl}^{\alpha_3}}{\omega_{bo} - \omega'} + \frac{d_{ob}^{\alpha_3} d_{bl}^{\alpha_1}}{\omega_{bo} - \omega''' + \omega} \right]^* = f_{-\omega', -\omega'''}^{*\alpha_1 \alpha_3} \quad (ii)$$

$$\Sigma \left[\frac{d_{ob}^{\alpha_2} d_{bl}^{\mu}}{\omega_{bl} + \omega' + \omega'' + \omega''' + \omega} + \frac{d_{ob}^{\mu} d_{bl}^{\alpha_2}}{\omega_{bl} - \omega''' + \omega} \right] = g_{\omega, -\omega''}^{\alpha_2 \mu} \quad (iii)$$

$$\Sigma \left[\frac{d_{ob}^{\alpha_3} d_{bl}^{\alpha_1}}{\omega_{bl} + \omega'} + \frac{d_{ob}^{\alpha_1} d_{bl}^{\alpha_3}}{\omega_{bl} + \omega''' + \omega} \right]^* = g_{\omega', \omega'''}^{*\alpha_3 \alpha_1} \quad (iv) \quad (4.56)$$

where $\omega = \omega' + \omega'' + \omega'''$ has been used for simplicity as before. Then

$$p_{\mu \alpha_1 \alpha_2 \alpha_3}^{\text{SRS-S(1)}} (-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \frac{1}{\omega_{10} - \omega - \omega''' - i\Gamma_{10}}$$

$$(\rho_{00}^{\circ} f_{-\omega, \omega''}^{\mu \alpha_2} f_{-\omega', -\omega'''}^{*\alpha_1 \alpha_3} - \rho_{11} g_{\omega, -\omega''}^{\alpha_2 \mu} g_{\omega', \omega'''}^{*\alpha_3 \alpha_1}) + \text{N.R.} \quad (4.57)$$

This can be generalized to include the effect of all the populated rotational levels

$$p_{\mu \alpha_1 \alpha_2 \alpha_3}^{\text{SRS-S(1)}} (-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3 J} \sum \frac{1}{\omega_{10J} - \omega - \omega''' - i\Gamma_{10J}}$$

$$(\rho_{00} f_{-\omega, \omega''}^{\mu \alpha_2} f_{-\omega', -\omega'''}^{*\alpha_1 \alpha_3} - \rho_{11} g_{\omega, -\omega''}^{\alpha_2 \mu} g_{\omega', \omega'''}^{*\alpha_3 \alpha_1})_J + \text{N.R.} \quad (4.58)$$

where ρ_{00}^o and ρ_{11}^o now represent the density matrix elements for individual rotational levels. Further, from Eq (3.43) if higher vibrational levels are populated due to higher temperatures, the corresponding terms for ρ_{11}^o and ρ_{22}^o are used and $p^{SRS-S(1)}$ becomes

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{SRS-S(1)}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v,J} \frac{1}{\omega_{v-vJ} - \omega' - \omega'' - i\Gamma_{v-vJ}} \quad (4.59)$$

$$(\rho_v f_{-\omega, \omega'}^{\mu\alpha_2}(v) f_{-\omega, \omega''}^{*\alpha_1\alpha_3}(v) - \rho_v g_{\omega, \omega'}^{\alpha_2\mu}(v') g_{\omega', \omega''}^{*\alpha_3\alpha_1}(v'))_J$$

$$\text{where } v' = v + 1 \quad (4.60)$$

$$\left[\begin{array}{c} f_{-\omega, \omega'}^{\mu\alpha_2}(v) \\ \end{array} \right]_J = \sum_b \left[\begin{array}{c} \frac{d_{vJb}^{\mu} d_{bv'J}^{\alpha_2}}{\omega_{bvJ} - \omega' - \omega'' - \omega''' +} + \frac{d_{vJb}^{\alpha_2} d_{bv'J}^{\mu}}{\omega_{bvJ} + \omega''} \\ \end{array} \right] \quad (4.61)$$

$$\left[\begin{array}{c} g_{\omega, \omega'}^{\alpha_2\mu}(v') \\ \end{array} \right]_J = \sum_b \left[\begin{array}{c} \frac{d_{vJb}^{\alpha_2} d_{bv'J}^{\mu}}{\omega_{bv'J} + \omega' + \omega'' + \omega''' +} + \frac{d_{vJb}^{\mu} d_{bv'J}^{\alpha_2}}{\omega_{bv'J} - \omega''} \\ \end{array} \right] \quad (4.62)$$

In Appendix F, the form of $\bar{p}^{SRS-S(1)}$ is obtained for the monochromatic fields, as given in Eq (4.6). Also, the relation between the f and g factors and the ordinary Raman polarizability is derived. It is also shown that for monochromatic fields tuned to a vibrational-rotational resonance the f and g factors become equal. This approximation is only valid as long as no electronic resonances occur. In the case of an electronic resonance, one of the denominators in Eq (4.56) would approach zero and the linewidths of the states could no longer be ignored. With the presence of the linewidth, the approximation of equal f and g factors (Appendix F) would not be

applicable. The restriction also holds for the form of the equations derived for ordinary Raman polarizabilities (Ref 83:120). For the experimental conditions of interest as defined by Eq (4.39), the equality of the f and g factors and their corresponding complex conjugates will apply. The results will be stated both with and without this approximation. In this manner, the results obtained with the addition of linewidth to the appropriate term may be used when electronic resonances are created.

This procedure to derive expressions for the third order polarizabilities can be followed for each process in Eq (4.45). This procedure is only repeated in detail for one more of the polarizabilities at ω_1 , $\overset{=}{p}^{\text{CARS}(1)}$. The remainder of the polarizabilities of Eq (4.45) are given without writing out all of the details. For $\overset{=}{p}^{\text{CARS}(1)}$, the field product is $\epsilon_1^*(-\omega')\epsilon_2(\omega'')\epsilon_3(\omega''')$ and from Table IV the resonant terms of Eq (4.21) are (i) through (viii) for ground state population. The effect of transition from other states can be incorporated as was done for Eq (4.59). There are now eight terms from Eq (4.21) with resonances. Four are associated with $(\omega_1-\omega_2)$ and four are associated with $(\omega_3-\omega_1)$. Because of these two associations, the derivation will be broken into two parts; one for each of the differences. First with $\alpha_1\omega'$, $\alpha_2\omega''$, $\alpha_3\omega'''$, by localization corresponding to $-\omega_1$, ω_2 , ω_3 , the term by term permutations for $(\omega_1-\omega_2)$ are:

Term (iii); $\alpha_1\alpha_2\mu\alpha_3$ and $\alpha_2\alpha_1\mu\alpha_3$

Term (iv); $\alpha_1\alpha_2\alpha_3\mu$ and $\alpha_2\alpha_1\alpha_3\mu$

Term (v); $\mu\alpha_3\alpha_1\alpha_2$ and $\mu\alpha_3\alpha_2\alpha_1$

Term (vi); $\alpha_3\mu\alpha_1\alpha_2$ and $\alpha_3\mu\alpha_2\alpha_1$

When linewidths for terms far from resonance are dropped Eq (4.21) provides

$$1p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}(1)}(-\omega; \omega', \omega'', \omega''') = -\frac{1}{6\hbar^3} \sum_{b,d} \rho_{00}^0$$

$$\left[\frac{d_{ob}^{\alpha_1} d_{bl}^{\alpha_2} d_{ld}^{\mu} d_{do}^{\alpha_3}}{(\omega_{ob} - \omega') (\omega_{ol} - \omega' - \omega''' - i\Gamma_{ol}) (\omega_{od} + \omega''')} \right]$$

$$+ \frac{d_{ob}^{\alpha_2} d_{bl}^{\alpha_1} d_{ld}^{\mu} d_{do}^{\alpha_3}}{(\omega_{ob} - \omega'') (\omega_{ol} - \omega'' - \omega' - i\Gamma_{ol}) (\omega_{od} + \omega''')}$$

$$+ \frac{d_{ob}^{\alpha_1} d_{bl}^{\alpha_2} d_{ld}^{\alpha_3} d_{do}^{\mu}}{(\omega_{ob} - \omega') (\omega_{ol} - \omega' - \omega''' - i\Gamma_{ol}) (\omega_{od} - \omega' - \omega''' - \omega''')}$$

$$+ \frac{d_{ob}^{\alpha_2} d_{bl}^{\alpha_1} d_{ld}^{\alpha_3} d_{do}^{\mu}}{(\omega_{ob} - \omega'') (\omega_{ol} - \omega'' - \omega' - i\Gamma_{ol}) (\omega_{od} - \omega'' - \omega' - \omega''')} + \text{N.R.}$$

$$+ \sum_{b,d} \rho_{11}^0 \left[\frac{d_{lb}^{\mu} d_{bo}^{\alpha_3} d_{od}^{\alpha_1} d_{dl}^{\alpha_2}}{(\omega_{lb} + \omega''' + \omega' + \omega'') (\omega_{lo} + \omega' + \omega''' + i\Gamma_{lo}) (\omega_{ld} + \omega'')} \right]$$

$$+ \frac{d_{lb}^{\mu} d_{bo}^{\alpha_3} d_{od}^{\alpha_2} d_{dl}^{\alpha_1}}{(\omega_{lb} + \omega''' + \omega' + \omega'') (\omega_{lo} + \omega' + \omega''' + i\Gamma_{lo}) (\omega_{ld} + \omega'')}$$

$$+ \frac{d_{lb}^{\alpha_3} d_{bo}^{\mu} d_{od}^{\alpha_1} d_{dl}^{\alpha_2}}{(\omega_{lb} - \omega''') (\omega_{lo} + \omega' + \omega''' + i\Gamma_{lo}) (\omega_{ld} + \omega'')}$$

$$+ \frac{d_{lb}^{\alpha_3} d_{bo}^{\mu} d_{od}^{\alpha_2} d_{dl}^{\alpha_1}}{(\omega_{lb} - \omega''') (\omega_{lo} + \omega'' + \omega' + i\Gamma_{lo}) (\omega_{ld} + \omega')} + \text{N.R.}$$

(4.63)

Equation (4.50) can be used to factor the resonant denominator from the terms of Eq (4.63). Then the bracketed terms of Eq (4.63) can be factored to yield, respectively

$$\left[\frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_2}}{(\omega_{ob} - \omega')} + \frac{d_{ob}^{\alpha_2} d_{b1}^{\alpha_1}}{(\omega_{ob} - \omega'')} \right] \times \left[\frac{d_{ld}^{\mu} d_{do}^{\alpha_3}}{(\omega_{od} + \omega''')} + \frac{d_{ld}^{\alpha_3} d_{do}^{\mu}}{(\omega_{od} - \omega' - \omega'' - \omega''')} \right] \quad (4.64)$$

$$\left[\frac{d_{lb}^{\mu} d_{bo}^{\alpha_3}}{(\omega_{lb} + \omega' + \omega'' + \omega''')} + \frac{d_{lb}^{\alpha_3} d_{bo}^{\mu}}{(\omega_{lb} - \omega''')} \right] \times \left[\frac{d_{od}^{\alpha_1} d_{dl}^{\alpha_2}}{(\omega_{ld} + \omega'')} + \frac{d_{od}^{\alpha_2} d_{dl}^{\alpha_1}}{(\omega_{ld} + \omega')} \right] \quad (4.65)$$

After changing the index in expression (4.65) from d to b and using $w_{ij} = -w_{ji}$ Eq (4.63) is

$$\begin{aligned} {}^1 P_{\mu \alpha_1 \alpha_2 \alpha_3}^{CARS(1)} (-\omega; \omega', \omega'', \omega''') &= \frac{1}{6\hbar^3} \frac{1}{(\omega_{lo} + \omega' + \omega'' + i\Gamma_{lo})} \\ &\times \sum_b \left[\frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_2}}{(\omega_{bo} + \omega')} + \frac{d_{ob}^{\alpha_2} d_{b1}^{\alpha_1}}{(\omega_{bo} + \omega'')} \right] \times \sum_b \left[\frac{d_{ob}^{\mu} d_{b1}^{\alpha_3}}{(\omega_{bo} + \omega' + \omega'' + \omega''')} + \frac{d_{ob}^{\alpha_3} d_{b1}^{\mu}}{(\omega_{bo} - \omega''')} \right]^* \\ &- p_{11}^o \sum_b \left[\frac{d_{ob}^{\alpha_2} d_{b1}^{\alpha_1}}{(\omega_{b1} - \omega')} + \frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_2}}{(\omega_{b1} - \omega'')} \right] \sum_b \left[\frac{d_{ob}^{\alpha_3} d_{b1}^{\mu}}{(\omega_{b1} - \omega' - \omega'' - \omega''')} + \frac{d_{ob}^{\mu} d_{b1}^{\alpha_3}}{\omega_{b1} + \omega'''} \right]^* \\ &+ N.R. \end{aligned} \quad (4.66)$$

If the f and g shorthand notation is used again,

$$f_{\omega', \omega''}^{\alpha_1 \alpha_2} = \sum_b \left[\frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_2}}{(\omega_{bo} + \omega')} + \frac{d_{ob}^{\alpha_2} d_{b1}^{\alpha_1}}{(\omega_{bo} + \omega'')} \right] \quad (i)$$

$$f_{\omega, -\omega}^{*\mu\alpha_3} = \sum_b \left[\frac{d_{ob}^\mu d_{bl}^{\alpha_3}}{(\omega_{bo} + \omega' + \omega'' + \omega''')} + \frac{d_{ob}^{\alpha_3} d_{bl}^\mu}{(\omega_{bo} - \omega''')} \right]^* \quad (\text{ii})$$

$$g_{-\omega', -\omega}^{*\alpha_2\alpha_1} = \sum_b \left[\frac{d_{ob}^{\alpha_2} d_{bl}^{\alpha_1}}{(\omega_{bl} - \omega')} + \frac{d_{ob}^{\alpha_1} d_{bl}^{\alpha_2}}{(\omega_{bl} - \omega'')} \right] \quad (\text{iii})$$

$$g_{-\omega, \omega}^{*\alpha_3\mu} = \sum_b \left[\frac{d_{ob}^{\alpha_3} d_{bl}^\mu}{(\omega_{bl} - \omega - \omega'' - \omega''')} + \frac{d_{ob}^\mu d_{bl}^{\alpha_3}}{(\omega_{bl} + \omega''')} \right]^* \quad (\text{iv}) \quad (4.67)$$

Thus, this part of p^{CARS} is

$$\begin{aligned} p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}(1)}(-\omega; \omega', \omega'', \omega''') &= \frac{1}{6\hbar^3} \frac{1}{\omega_{10} + \omega' + \omega'' + i\Gamma_{10}} \\ (\rho_{00}^0 f_{\omega', \omega}^{\alpha_1\alpha_2} f_{\omega', -\omega}^{*\mu\alpha_3} - \rho_{11}^0 g_{-\omega', -\omega}^{\alpha_2\alpha_1} g_{-\omega, \omega}^{*\alpha_3\mu}) &+ \text{N.R.} \quad (4.68) \end{aligned}$$

or for arbitrary vibrational-rotational population distribution

$$\begin{aligned} {}^1 p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}(1)}(-\omega; \omega', \omega'', \omega''') &= \frac{1}{6\hbar^3} \sum_{v,j} \frac{1}{\omega_{vvj} + \omega' + \omega'' + i\Gamma_{vvj}} \\ \times (\rho_v^0 f_{\omega', \omega}^{\alpha_1\alpha_2}(v) f_{\omega, -\omega}^{*\mu\alpha_3}(v) - \rho_{v'}^0 g_{-\omega', -\omega}^{\alpha_2\alpha_1}(v') g_{-\omega, \omega}^{*\alpha_3\mu}(v'))_j &+ \text{N.R.} \quad (4.69) \end{aligned}$$

with the appropriate definitions of f and g as in Eqs (4.61) and (4.62).

The term by term permutation for $(\omega_3 - \omega_1)$ is:

Term (i); $\mu\alpha_2\alpha_1\alpha_3$ and $\mu\alpha_2\alpha_3\alpha_1$

Term (ii); $\alpha_2\mu\alpha_1\alpha_3$ and $\alpha_2\mu\alpha_3\alpha_1$

Term (vii); $\alpha_1\alpha_3\mu\alpha_2$ and $\alpha_3\alpha_1\mu\alpha_2$

Term (viii); $\alpha_1\alpha_3\alpha_2\mu$ and $\alpha_3\alpha_1\alpha_2\mu$

Again dropping the linewidths from those terms far from resonance,

Eq (4.21) gives the resonance form

$$^2P_{\mu\alpha_1\alpha_2\alpha_3}^{CARS(1)}(-\omega; \omega', \omega'', \omega''') = -\frac{1}{6\hbar^3}$$

$$\left(\sum_{bd} P_{00}^0 \right) \left[\frac{d_{ob}^\mu d_{b1}^{\alpha_2} d_{1d}^{\alpha_1} d_{do}^{\alpha_3}}{(\omega_{ob} + \omega'' + \omega' + \omega''') (\omega_{o1} + \omega' + \omega''' + i\Gamma_{10}) (\omega_{od} + \omega'')} \right]$$

$$+ \frac{d_{ob}^\mu d_{b1}^{\alpha_2} d_{1d}^{\alpha_3} d_{do}^{\alpha_1}}{(\omega_{ob} + \omega'' + \omega''' + \omega') (\omega_{o1} + \omega''' + \omega' + i\Gamma_{10}) (\omega_{od} + \omega')}$$

$$+ \frac{d_{ob}^{\alpha_2} d_{b1}^\mu d_{1d}^{\alpha_1} d_{do}^{\alpha_3}}{(\omega_{ob} - \omega'') (\omega_{o1} + \omega' + \omega''' + i\Gamma_{10}) (\omega_{od} + \omega''')}$$

$$+ \frac{d_{ob}^{\alpha_2} d_{b1}^\mu d_{1d}^{\alpha_3} d_{do}^{\alpha_1}}{(\omega_{ob} - \omega'') (\omega_{o1} + \omega''' + \omega' + i\Gamma_{10}) (\omega_{od} + \omega')} + N.R. \quad] \quad +$$

$$\begin{aligned}
& + \sum_{bd} \rho_{11}^0 \left[\frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3} d_{od}^\mu d_{dl}^{\alpha_2}}{(\omega_{1b} - \omega') (\omega_{10} - \omega' - \omega''' - i\Gamma_{10}) (\omega_{1d} + \omega''')} \right. \\
& + \frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1} d_{od}^\mu d_{dl}^{\alpha_2}}{(\omega_{1b} - \omega''') (\omega_{10} - \omega''' - \omega' - i\Gamma_{10}) (\omega_{1d} + \omega''')} \\
& + \frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3} d_{od}^{\alpha_2} d_{dl}^\mu}{(\omega_{1b} - \omega') (\omega_{10} - \omega''' - \omega' - i\Gamma_{10}) (\omega_{1d} - \omega''' - \omega' - \omega''')} \\
& + \frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1} d_{od}^{\alpha_2} d_{dl}^\mu}{(\omega_{1b} - \omega''') (\omega_{10} - \omega''' - \omega' - i\Gamma_{10}) (\omega_{1d} - \omega''' - \omega' - \omega'')} \\
& \left. + N.R. \right] \quad (4.70)
\end{aligned}$$

The resonant denominator is factored by using Eq (4.50). The bracketed terms in Eq (4.70) are factored, respectively, to

$$\left[\frac{d_{ob}^\mu d_{bl}^{\alpha_2}}{(\omega_{ob} + \omega' + \omega''' + \omega''')} + \frac{d_{ob}^{\alpha_2} d_{bl}^\mu}{(\omega_{ob} - \omega''')} \right] \left[\frac{d_{1d}^{\alpha_1} d_{do}^{\alpha_3}}{(\omega_{od} + \omega''')} + \frac{d_{1d}^{\alpha_3} d_{do}^{\alpha_1}}{(\omega_{od} + \omega')} \right] \quad (4.71)$$

$$\left[\frac{d_{1b}^{\alpha_1} d_{bo}^{\alpha_3}}{(\omega_{1b} - \omega')} + \frac{d_{1b}^{\alpha_3} d_{bo}^{\alpha_1}}{(\omega_{1b} - \omega''')} \right] \left[\frac{d_{od}^{\alpha_2} d_{dl}^\mu}{(\omega_{1d} - \omega' - \omega''' - \omega''')} + \frac{d_{od}^\mu d_{dl}^{\alpha_2}}{(\omega_{1d} + \omega''')} \right] \quad (4.72)$$

The index change from d to b and $\omega_{ij} = -\omega_{ji}$ as before reduces Eq (4.70) to

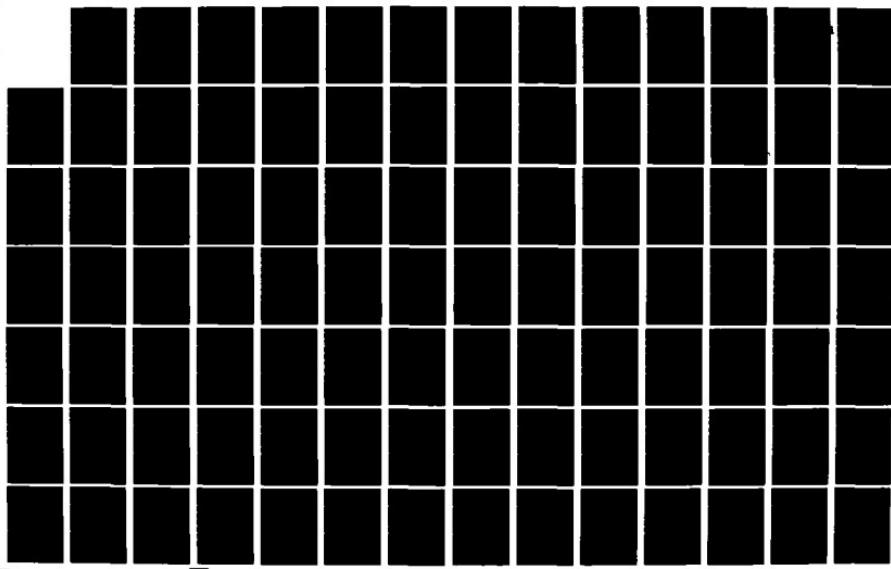
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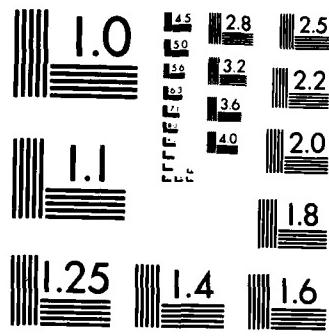
THIRD ORDER POLARIZATION FOR MULTIFREQUENCY COHERENT
ANTI-STOKES RAMAN SCATTERING(U) AIR FORCE INST OF TECH
WRIGHT-PATTERSON AFB OH SCHOOL OF ENGI. R F WEBER
UNCLASSIFIED SEP 82 AFIT/DS/PH/82-2

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MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963 A

$$^2 p_{\alpha_1 \alpha_2 \alpha_3}^{CARS} (-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \frac{1}{\omega_{l_0} - \omega' - \omega'' - i\Gamma_{l_0}}$$

$$\begin{aligned} & \times \left\{ \rho_{00}^0 \sum_b \left[\frac{d_{ob}^\mu d_{b1}^{\alpha_2}}{(\omega_{bo} - \omega' - \omega'' - \omega''')} + \frac{d_{ob}^{\alpha_2} d_{b1}^\mu}{(\omega_{bo} + \omega'')} \right] \times \sum_b \left[\frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_3}}{(\omega_{bo} - \omega')} + \frac{d_{ob}^{\alpha_3} d_{b1}^{\alpha_1}}{(\omega_{bo} - \omega''')} \right]^* \right. \\ & - \rho_{11}^0 \sum_b \left[\frac{d_{ob}^{\alpha_2} d_{b1}^\mu}{(\omega_{b1} + \omega' + \omega'' + \omega''')} + \frac{d_{ob}^\mu d_{b1}^{\alpha_2}}{(\omega_{b1} - \omega'')} \right] \times \sum_b \left[\frac{d_{ob}^{\alpha_3} d_{b1}^{\alpha_1}}{(\omega_{b1} + \omega')} + \frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_3}}{(\omega_{b1} - \omega''')} \right]^* \\ & \left. \right\} + N.R. \end{aligned} \quad (4.73)$$

With the f and g factors defined as

$$f_{-\omega, \omega''}^{\mu \alpha_2} = \sum_b \left[\frac{d_{ob}^\mu d_{b1}^{\alpha_2}}{(\omega_{bo} - \omega' - \omega'' - \omega''')} + \frac{d_{ob}^{\alpha_2} d_{b1}^\mu}{(\omega_{bo} + \omega'')} \right] \quad (i)$$

$$f_{-\omega, -\omega'''}^{*\alpha_1 \alpha_3} = \sum_b \left[\frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_3}}{(\omega_{bo} - \omega')} + \frac{d_{ob}^{\alpha_3} d_{b1}^{\alpha_1}}{(\omega_{bo} - \omega''')} \right]^* \quad (ii)$$

$$g_{\omega, -\omega''}^{\alpha_2 \mu} = \sum_b \left[\frac{d_{ob}^{\alpha_2} d_{b1}^\mu}{(\omega_{b1} + \omega' + \omega'' + \omega''')} + \frac{d_{ob}^\mu d_{b1}^{\alpha_2}}{(\omega_{b1} - \omega'')} \right] \quad (iii)$$

$$g_{\omega', -\omega'''}^{*\alpha_3 \alpha_1} = \sum_b \left[\frac{d_{ob}^{\alpha_3} d_{b1}^{\alpha_1}}{(\omega_{b1} + \omega')} + \frac{d_{ob}^{\alpha_1} d_{b1}^{\alpha_3}}{(\omega_{b1} - \omega''')} \right]^* \quad (iv)$$

Eq (4.73) is

$${}^2 p_{\mu \alpha_1 \alpha_2 \alpha_3}^{\text{CARS}(1)} (-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \frac{1}{\omega_{10} - \omega' - \omega''' - i\Gamma_{10}} \\ (\rho_{00}^0 f_{-\omega, \omega''}^{\mu \alpha_2} f_{-\omega', -\omega'''}^{*\alpha_1 \alpha_3} - \rho_{11}^0 g_{\omega, -\omega''}^{\alpha_2 \mu} g_{\omega', -\omega'''}^{*\alpha_3 \alpha_1}) + \text{N.R.} \quad (4.75)$$

or, in general

$${}^2 p_{\mu \alpha_1 \alpha_2 \alpha_3}^{\text{CARS}(1)} (-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v, J} \frac{1}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}} \\ \times (\rho_v^0 f_{-\omega, \omega''}^{\mu \alpha_2} (v) f_{-\omega', -\omega'''}^{*\alpha_1 \alpha_3} (v) - \rho_{11}^0 g_{\omega, -\omega''}^{\alpha_2 \mu} (v') g_{\omega', -\omega'''}^{*\alpha_3 \alpha_1} (v')) J \\ + \text{N.R.} \quad (4.76)$$

The results given by Eqs (4.68) and (4.75) can now be added together to form the complete CARS polarizability for Eq (4.45).

$$p_{\mu \alpha_1 \alpha_2 \alpha_3}^{\text{CARS}(1)} (-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \\ \left[\frac{\rho_{00}^0 f_{-\omega, \omega''}^{\alpha_1 \alpha_2} f_{-\omega', -\omega'''}^{*\mu \alpha_3} - \rho_{11}^0 g_{-\omega', -\omega''}^{\alpha_2 \alpha_1} g_{-\omega, \omega'''}^{*\alpha_3 \mu}}{\omega_{10} + \omega' + \omega''' + i\Gamma_{10}} \right. \\ \left. + \frac{\rho_{00}^0 f_{-\omega, \omega''}^{\mu \alpha_2} f_{-\omega', -\omega'''}^{*\alpha_1 \alpha_3} - \rho_{11}^0 g_{\omega, -\omega''}^{\alpha_2 \mu} g_{\omega', -\omega'''}^{*\alpha_3 \alpha_1}}{\omega_{10} - \omega' - \omega''' - i\Gamma_{10}} \right] \\ + \text{N.R.} \quad (4.77)$$

The generalized expression for $p^{\text{CARS}(1)}$ may be similarly obtained by the addition of Eqs (4.69) and (4.76). The monochromatic result, from Eq (4.77) with the resonant approximation for equality of f and g is

$$\begin{aligned}
 \text{CARS } p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega_1; -\omega_1, \omega_2, \omega_3) &= \frac{1}{6\hbar^3} (\rho_{00}^0 - \rho_{11}^0) \left[\frac{f^{\alpha_1\alpha_2} f^{*\mu\alpha_3}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} \right. \\
 &\quad \left. + \frac{f^{\mu\alpha_2} f^{*\alpha_1\alpha_3}}{\omega_{10} + \omega_1 - \omega_3 - i\Gamma_{10}} \right] + \text{N.R.} \tag{4.78}
 \end{aligned}$$

Equation (4.78) may also be written as a function of the Raman polarizabilities, p_{ij} , in a manner similar to Appendix F. When the equivalence of $(\omega_1 - \omega_2)$ and $(\omega_3 - \omega_1)$ near resonance are used, the monochromatic CARS polarizability becomes

$$\begin{aligned}
 \text{CARS } p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega_1; -\omega_1, \omega_2, \omega_3) &= \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \left[\frac{p_{\mu\alpha_3}^{\omega_3} p_{\alpha_2\alpha_1}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} + \frac{p_{\alpha_1\alpha_3}^{\omega_3} p_{\alpha_2\mu}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}} \right] \\
 &\quad + \text{N.R.} \tag{4.79}
 \end{aligned}$$

Two factors are of interest in this expression. First, the Raman polarizabilities are not only indexed differently as in the case of SRS-S(1) but also occur at different frequencies, ω_1 and ω_3 . Second, when the component of the dipole moment, μ , is aligned with the component of the field $\epsilon_1^*(-\omega)$, α_1 , the products of the polarizabilities are equal and Eq (4.79) may be written as

$$\begin{aligned}
 \text{CARS } p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega_1; -\omega_1, \omega_2, \omega_3) &= \frac{(\rho_{00}^0 - \rho_{11}^0)}{6M} \left[\frac{p_{\mu\alpha_3}^{\omega_3} p_{\alpha_2\mu}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} \right] \left[\frac{2(\omega_{10} - \omega_1 + \omega_2)}{(\omega_{10} - \omega_1 + \omega_2)^2 + \Gamma^2} \right] \\
 &\quad + \text{N.R.} \tag{4.80}
 \end{aligned}$$

Since the dipole matrix elements in p_{ij} are real in the dipole approximation (see Appendix E), this polarizability is real.

The following observation is made on the effect of intrinsic permutation symmetry not only for CARS and SRS-S polarizabilities derived above, but for the other third order polarizabilities as well.

Although intrinsic permutation symmetry applies, $p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)} = p_{\mu\alpha_2\alpha_1\alpha_3}^{(3)} =$ etc., the form of the derived expression for $p^{(3)}$ (e.g., Eqs (4.57) and (4.77)) is fixed and will not change as $\alpha_1\omega'$, $\alpha_2\omega''$, $\alpha_3\omega'''$ are permuted. This occurs since the resonance effect will select from the six possible permutations of the terms in the full polarizability expression, Eq (4.21), the identical terms for each permutation set. Therefore, $p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}(1)}(-\omega; \omega', \omega'', \omega''')$ is given by Eq (4.77) but so are all other $p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}(1)}$ created by permutation.

By repeating the procedure performed for the SRS-S and CARS polarizabilities, expressions for SRS-P, CSRS, and CMRS polarizabilities in Eq (4.45) may be derived. Since this is straight forward, it will not be performed in detail. The other third order polarizabilities in Eq (4.46), (4.47) and (4.48) can also be obtained by exactly the same approach as for the SRS-S and CARS polarizabilities at ω_1 . Since there is no new information to be gained in repeating the procedure, only the results are presented. Appendix G contains tables of the required polarizability expressions. These polarizabilities are presented for each of the central frequencies, $\omega_1, \omega_2, \omega_3$ and ω_4 , in four tables;

- (1) Multifrequency and multiresonant, $f \neq g$
- (2) Multifrequency and multiresonant with Raman polarizability, $f = g$

- (3) Monochromatic and single resonance, $f = g$
- (4) Monochromatic and single resonance with Raman polarizability
 $f = g$

Application Considerations

From the equations for the third order resonant polarizabilities given in Appendix G, it is, in principle, possible to compute the required set of third order polarizabilities. To perform this computation does require the complete set of state functions that describe the molecular system. These are necessary to obtain the energy levels of interest, ω_{V-VJ} and the factors f and g. In these latter two terms, the sum in Eqs (4.61) and (4.62) are over all states of the molecule. In practice, this information is not available for even the simpler molecules. It is therefore necessary to find a way to express either the polarizabilities or the resultant susceptibilities in terms of measurable parameters.

The use of the Raman polarizabilities in the third order polarizability equations of Appendix G is one approach to finding useful experimental parameters. It was shown in Appendix F that for the monochromatic case, the f and g factors can be related to the Raman polarizabilities. In the multifrequency case, this same relationship can be used as a reasonable approximation. The states of the summation can be considered for two situations. One, when the applied field frequencies are near the vibrational-rotational resonance in which case the results of Appendix F are applicable. The second situation is when the applied field frequencies are far from the resonance. In this case, ω_{bo} may be approximated as ω_{b1} where ω_V is

neglected as small compared to $(\omega_1 - \omega_2)$. Thus, the Raman polarizabilities replace f and g with a general form of $p_{\sigma\sigma}^{\omega}$. These Raman polarizabilities can be combined to form invariants to the rotation of the molecular axes. These polarizability invariants are:

(1) The average (or mean) polarizability, a

(2) The anisotropy, γ

(3) The antisymmetry, δ

where

$$a = \frac{1}{3} (p_{11} + p_{22} + p_{33}) \quad (4.81)$$

$$\begin{aligned} \gamma^2 = & \frac{1}{2} \left[(p_{11}-p_{22})^2 + (p_{22}-p_{33})^2 + (p_{33}-p_{11})^2 \right. \\ & \left. + \frac{3}{2} \left\{ (p_{12}+p_{21})^2 + (p_{23}+p_{32})^2 + (p_{31}+p_{13})^2 \right\} \right] \end{aligned} \quad (4.82)$$

$$\delta^2 = \frac{3}{4} \left[(p_{12}-p_{21})^2 + (p_{23}-p_{32})^2 + (p_{31}-p_{13})^2 \right] \quad (4.83)$$

(Ref 83:121).

In general, the Raman polarizability tensor may be a complex quantity but this requires that the wave functions describing the molecule must also be complex. Complex wave functions will exist only with the presence of an external magnetic field or with internal magnetic perturbations (e.g., spin-orbit interaction). With the electric dipole interaction assumption of Chapter II, the wave

functions in use here are real since the dipole operator is a linear operator and its expectation value represents a real physical quantity (i.e., the operator is Hermitian (Ref 89:89)). This places no restrictions on the frequency denominators in p_{ij} , $\omega_{bf} + \omega$ and $\omega_{bi} - \omega$, which near a resonance must include a complex quantity, $i\Gamma$, for damping. For real wavefunctions, the equality

$$d_{ob}^\sigma = d_{bo}^\sigma \quad (4.84)$$

has been shown to occur (Appendix E). However, even with real wavefunctions the equality

$$d_{ob}^\sigma = d_{ob}^\rho \quad (4.85)$$

when $\sigma \neq \rho$ depends on the specific molecule. Therefore in general

$$p_{\rho\sigma} \neq p_{\sigma\rho} \quad (4.86)$$

and the Raman polarizability tensors are not, in general, symmetric.

Then \bar{p} can be written as

$$\bar{p} = \bar{p}_{\text{isotropic}} + \bar{p}_{\text{anisotropic}} + \bar{p}_{\text{antisymmetric}} \quad (4.87)$$

For this nonsymmetric case, all three of the polarizability invariants are required. This situation occurs when there is electronic resonant enhancement of the Raman active resonant third order process.

A symmetric form for the Raman polarizability tensor and hence the third order polarizabilities does exist under a special set of conditions. Placzek (Ref 15) determined that p_{ij} is symmetric when all of the following conditions apply:

- (1) The frequency of the incident field is much greater than the

frequency representing any vibration or rotation transition of the molecule.

(2) The frequency of the incident field is much less than the frequency representing any electronic transition of the molecule.

(3) The ground electronic state is not degenerate.

These conditions are met for many of the CARS and other third order experiments performed, especially those on diatomic molecules. Thus, when the above conditions are included with those assumptions already made, the Raman polarizability tensor is both real and symmetric,

$$p_{xy} = p_{yx} \quad (4.88)$$

And, only the polarizability invariants α and γ are required. The third order polarizabilities in Appendix G can then make use of Eq (4.88) under these conditions.

A further simplification is possible when there is no electronic resonance. In this case, the frequency dependence of the Raman polarizability can be neglected with the result that

$$p_{ij}^{\omega_1} \approx p_{ij}^{\omega_2} \approx p_{ij}^{\omega_3} \approx p_{ij}^{\omega_4} \quad (4.89)$$

Upon examination of the equations for the third order polarizabilities in Appendix G certain relationships exist which are independent of the symmetry or electronic resonant enhancement. One of these is

$$\begin{aligned} p^{\text{SRS-S(1)}} &= p^{\text{*SRS-S(2)}} \\ p^{\text{SRS-P(1)}} &= p^{\text{*SRS-P(3)}} \\ p^{\text{SRS-SS(2)}} &= p^{\text{*SRS-SS(4)}} \end{aligned} \quad (4.90)$$

Another relationship that exists when two of the frequency arguments of the polarizability are the same is

$$p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = p_{\mu\alpha_1\alpha_3\alpha_2}(-\omega; \omega', \omega'', \omega''') \quad (4.91)$$

This occurs for for $p^{\text{CSRS}(1)}$, $p^{\text{CARS}(2)}$, $p^{\text{CARS}(3)}$, and $p^{\text{CSRS}(4)}$. These relationships and those for the Raman polarizability can be used to simplify results of orientation averaging and to obtain dependence on experimental parameters.

The third order polarizability equations of Appendix G show that in general the isotropic conditions which must apply for a gas do not apply to the polarizabilities unless orientational averaging is performed to obtain the susceptibilities as in Eq (3.22). Or, unless the f (or p_{ij}) terms contain the specific symmetry to allow this to occur. The isotropic conditions (Ref 48:49) are:

(1) There are 21 nonzero elements of the 81 possible $\bar{x}^{(3)}$ tensor elements. These have the form; $x_{iiii}^{(3)}$, $x_{iiji}^{(3)}$, $x_{ijij}^{(3)}$, $x_{ijji}^{(3)}$ where $i,j=1,2,3$.

(2) Only three elements of the twenty one tensor elements are independent because of the equalities; $x_{iiji}^{(3)}$ are all equal, $x_{ijij}^{(3)}$ are all equal, $x_{ijji}^{(3)}$ are all equal, $x_{iiii}^{(3)}$ are all equal, and

$$x_{iiii}^{(3)} = x_{iiji}^{(3)} + x_{ijij}^{(3)} + x_{ijji}^{(3)} \quad (4.92)$$

This latter equality is normally written as

$$x_{1111}^{(3)} = x_{1122}^{(3)} + x_{1212}^{(3)} + x_{1221}^{(3)} \quad (4.93)$$

That these conditions do not hold in the absence of orientational

averaging can be shown by examining any individual $p_{ij}^{(3)}$ term which would be proportional to $\chi^{(3)}$. Since the resonant term is the largest, only it needs to be considered. As an example, use SRS-S(1) $p_{\alpha_1 \alpha_2 \alpha_3}^{SRS-S(1)} (-\omega; -\omega_2, \omega_2, \omega_1)$ from Table G IV.

$$p_{1111}^{SRS-S(1)} = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{11}p_{11}}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}} \quad (4.94)$$

and

$$p_{1122}^{SRS-S(1)} + p_{1212}^{SRS-S(1)} + p_{1221}^{SRS-S(1)} = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{1}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}} \\ \times (p_{12}p_{21} + p_{22}p_{11} + p_{21}p_{21}) \quad (4.95)$$

where the real quality of p_{ij} has been used. If the symmetric relation for p_{ij} is used in Eq (4.93), then the equality

$$p_{11}p_{11} = 2p_{12}p_{12} + p_{11}p_{22} \quad (4.96)$$

must hold for the isotropic condition. This is only true if $p_{12} = 0$ and $p_{22} = p_{11}$. But, then $p_{1122} = 0$ and $p_{1221} = 0$ under all conditions. This violates the first of the isotropic conditions. Therefore, orientational averaging must be used to obtain the correct form of the susceptibility in a gas. This averaging is performed in Chapter VI for the susceptibilities required.

One last consideration must be given to the use of the Raman scattering cross section as an experimental parameter. In Chapter III, the classical derivation showed how this cross section could be used to determine the third order polarizabilities. However, as was discussed there and is represented in the equations of this chapter,

the frequency dependence can play an important part in this. It is therefore important to have a derivation of the Raman scattering cross section that is consistent with that of the third order polarizabilities. Such a derivation is performed in Chapter V using quantum-mechanical theory.

V. Raman Scattering Cross Section

Equations

The Raman scattering cross section, σ , is a measure of the amount of energy removed from an incident light beam by the Raman process. The differential Raman cross section, $\frac{d\sigma}{d\Omega}$, is a measure of the energy scattered into an element of the solid angle, $d\Omega$. As such, it is one of the parameters measured to describe the Raman process. In Chapter III, it was shown that the differential cross section (since only the Raman cross section is being considered, the description Raman is dropped) can be related to the third order susceptibility in the classical theory. But, information on the frequency dependence was not directly available. This frequency dependence can be introduced directly by deriving the differential cross section using a quantum theory approach. Loudon (Ref 70:267) has presented a theoretical approach where both the molecular system and radiation field are quantized. While this deviates from the semiclassical approach used in previous chapters, the simplicity of the derivation dictates its use here. The derivation presented here for the ordinary Raman scattering follows this second order perturbation approach. From the general differential cross section derived, different forms of the cross section are obtained and discussed. In addition, scaling of the differential cross section with vibrational level is presented.

To determine the cross section for light scattered from an atom, the photon scattering cross section is defined as

$$\sigma = \frac{V}{nc} \frac{1}{\tau} \quad (5.1)$$

where

V = volume

n = mean number of photons

$\frac{1}{\tau}$ = transition probability per unit time or transition rate

The probability of being in a final state of a system given an initial state is determined by the matrix element of the system time development operator between these two states. The transition rate from the initial state to the final state is equal to the time derivative of this matrix element. An equation for this transition rate obtained using the second order perturbation theory is

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_F \sum_{k_s} \left| \langle F | \hat{H}_{NL} | I \rangle + \frac{1}{\hbar} \sum_B \frac{\langle F | \hat{H}_1 | B \rangle \langle B | \hat{H}_1 | I \rangle}{\omega_U - \omega_B} \right|^2 \times \delta(\omega_U - \omega_F) \quad (5.2)$$

where

F = state vector for the combined molecular and radiation system final state.

I = state vector for the combined molecular and radiation system initial state

B = state vector for eigenstates of the unperturbed system forming a complete set

\hat{H}_{NL} = nonlinear contribution to the interaction Hamiltonian

\hat{H}_1 = electric dipole term of the interaction Hamiltonian

k, k_s = wavevector of incident and scattered light, respectively

ω, ω_s = frequency of incident and scattered light, respectively

$M(\omega_U - \omega_F)$ = energy difference between initial and final state of the system

n, n_s = number of photons at frequencies ω and ω_s present

$\delta(\omega_U - \omega_F)$ = a density of states

The contribution of the nonlinear Hamiltonian is shown to be negligible with respect to that from H and can be neglected (Ref 70:282).

The state vectors can be written as

$$|B\rangle = |n, n_s, b\rangle \quad (5.3)$$

Since the cross section is independent of the photon distribution, the derivation may be simplified by specifying a definite number of photons. Thus

$$\begin{aligned} |I\rangle &= |n, 0, i\rangle \\ |F\rangle &= |n-1, 1, f\rangle \end{aligned} \quad (5.4)$$

The diagrammatic representation of the two processes that contribute in the dipole approximation are shown in Figure 6. From this figure,

$$\omega_U = \omega_i + n\omega \quad (5.5)$$

$$\omega_F = \omega_f + \omega_s + (n-1)\omega \quad (5.6)$$

based on the mean number of photons in Eq (5.4). When Eq (5.6) is subtracted from Eq (5.5), the result is

$$\omega_U - \omega_F = \omega - \omega_s - \omega_{fi} \quad (5.7)$$

where $\omega_{fi} = \omega_f - \omega_i$. Similarly, $\omega_U - \omega_B$ is obtained from Figure 6. as

$$\text{diagram (a): } \omega_U - \omega_B = \omega_i + n\omega - \omega_b - (n-1)\omega = \omega - \omega_{bi} \quad (5.8)$$

$$(b): \omega_U - \omega_B = \omega_i + n\omega - \omega_b - n\omega - \omega_s = \omega_{ib} - \omega_s \quad (5.9)$$

From this information, Eq (5.2) can be written as

$$\frac{1}{\tau} = \frac{2\pi}{\hbar^2} \sum_f \sum_{k_s} \left| \frac{1}{\hbar} \sum_b \frac{\langle n-1, 1, f | \hat{H}_1 | n-1, 0, b \rangle \langle n-1, 0, b | \hat{H}_1 | n, 0, i \rangle}{\omega - \omega_{bi}} \right. \right. \\ \left. \left. + \sum_b \frac{\langle n-1, 1, f | \hat{H}_1 | n, 1, b \rangle \langle n, 1, b | \hat{H}_1 | n, 0, i \rangle}{\omega_{ib} - \omega_s} \right|^2 \right. \\ \times \delta(\omega - \omega_s - \omega_{fi}) \quad (5.10)$$

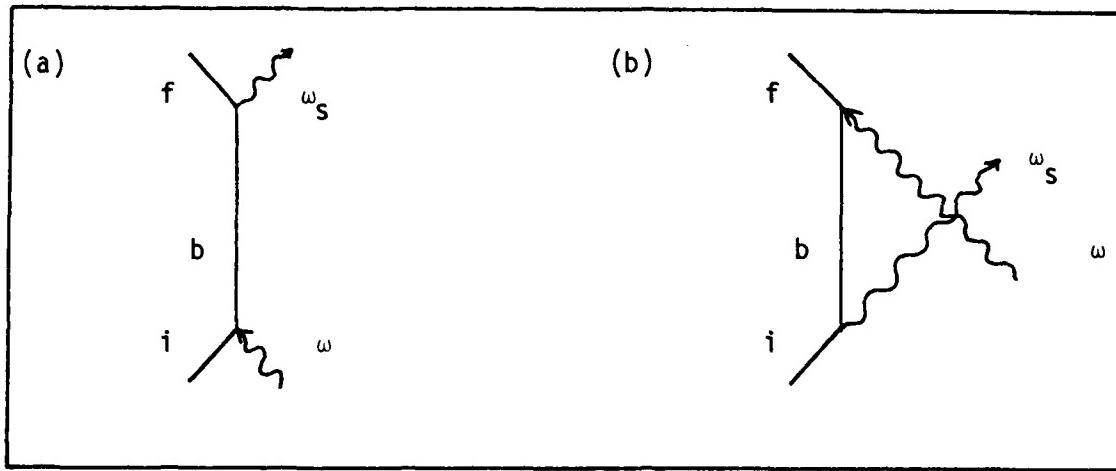


Figure 6 - Diagrams for the Two Dipole Interaction Contributions to the Raman Scattering Process

For this situation, \hat{H}_1 is given by (Ref 70:182)

$$\hat{H}_1 = i \sum_K \sum_{m,j} \left(\frac{2\pi\hbar\omega}{K} \right)^{1/2} \bar{d}_{mj} (\hat{a}_K \hat{A}_K - \hat{a}_K^* \hat{A}_K^+) \hat{B}_m^+ \hat{B}_j \quad (5.11)$$

where

$$\bar{K} = \bar{k}, \bar{k}_s$$

$\hat{B}_m^{\dagger} \hat{B}_j$ = creation and destruction operator pair for the molecular states, $|m\rangle\langle j|$, such that

$$\hat{B}_m^{\dagger} \hat{B}_j |i\rangle = |m\rangle \delta_{ji} \quad (5.12)$$

$\hat{A}_K^{\dagger}, \hat{A}_K$ = creation and destruction operators for a photon in the mode K

$$\hat{A}_K^{\dagger} |n_K\rangle = (n_K + 1)^{1/2} |n_K + 1\rangle \quad (5.13)$$

$$\hat{A}_K |n_K\rangle = (n_K)^{1/2} |n_K - 1\rangle \quad (5.14)$$

\hat{a} = Unit polarization vector

Upon substitution of Eq (5.11) into Eq (5.10) the terms become;

(i) For $K = k_s$ ($\hat{a}_s^* \hat{A}_s^{\dagger}$), $m = f$, $j = b$

$$\langle n-1, 1, f | \hat{H}_1 | n-1, o, b \rangle = i \langle n-1, 1, f | n-1, 1, f \rangle$$

$$x \left(\frac{2\pi\hbar\omega_s}{V} \right)^{1/2} \hat{a}_s^* \cdot \vec{d}_{fb} \quad (5.15)$$

(ii) For $K = k$ ($\hat{a} \hat{A}$), $m = b$, $j = i$

$$\langle n-1, o, b | \hat{H}_1 | n, o, i \rangle = i \langle n-1, o, b | n-1, o, b \rangle$$

$$x \left(\frac{2\pi\hbar\omega}{V} \right)^{1/2} n^{1/2} \hat{a} \cdot \vec{d}_{bi} \quad (5.16)$$

(iii) For $K = k$, $m = f$, $j = b$

$$\begin{aligned} \langle n-1, 1, f | \hat{H}_1 | n, 1, b \rangle &= i \langle n-1, 1, f | n-1, 1, f \rangle \\ &\times \left(\frac{2\pi\hbar\omega}{V} \right)^{1/2} n^{1/2} \hat{a} \cdot \vec{d}_{fb}^- \end{aligned} \quad (5.17)$$

(iv) For $K = k_s$, $m = b$, $j = i$

$$\begin{aligned} \langle n, 1, b | \hat{H}_1 | n, 0, i \rangle &= i \langle n, 1, b | n, 1, b \rangle \\ &\times \left(\frac{2\pi\hbar\omega_s}{V} \right)^{1/2} \hat{a}_s^* \cdot \vec{d}_{bi}^- \end{aligned} \quad (5.18)$$

All other values from the summation will be zero due to the orthogonality of the system state vector. With these terms, Eq (5.10) simplifies to

$$\begin{aligned} \frac{1}{\tau} &= \frac{2\pi}{\hbar^2} \sum_f \sum_{k_s} \left| \frac{1}{\hbar} \sum_b \frac{\frac{i^2 2\pi\hbar}{V} (\omega\omega_s n)^{1/2} (\hat{a}_s^* \cdot \vec{d}_{fb}) (\hat{a} \cdot \vec{d}_{bi}^-)}{\omega - \omega_{bi}} \right. \\ &+ \left. \sum_b \frac{\frac{i^2 2\pi\hbar}{V} (\omega\omega_s n)^{1/2} (\hat{a} \cdot \vec{d}_{fb}) (\hat{a}_s^* \cdot \vec{d}_{bi}^-)}{\omega_{ib} - \omega_s} \right| \\ &\times \delta(\omega - \omega_s - \omega_{fi}) \end{aligned} \quad (5.19)$$

$$\begin{aligned} \frac{1}{\tau} &= \sum_{f, k_s} \frac{(2\pi)^3}{V^2 \hbar^2} n \omega \omega_s \left| \sum_b \frac{(\hat{a}_s^* \cdot \vec{d}_{fb})(\hat{a} \cdot \vec{d}_{bi}^-)}{\omega_{bi} - \omega} + \sum_b \frac{(\hat{a} \cdot \vec{d}_{fb})(\hat{a}_s^* \cdot \vec{d}_{bi}^-)}{\omega_{bi} + \omega_s} \right| \\ &\times \delta(\omega - \omega_s - \omega_{fi}) \end{aligned} \quad (5.20)$$

To put this in the form of the Raman polarizability tensor, ρ_{ij} , (Appendix F, Eq (F18)), Eq (5.20) can be rearranged to yield

$$\frac{1}{\tau} = \sum_{f, k_s} \frac{(2\pi)^3}{V^2 \hbar^2} n \omega_s \left| b \left[\frac{(\hat{a} \cdot \vec{d}_{fb})(\hat{a}_s^* \cdot \vec{d}_{bi})}{\omega_{bi} + \omega_s} + \frac{(\hat{a}_s^* \cdot \vec{d}_{fb})(\hat{a} \cdot \vec{d}_{bi})}{\omega_{bi} - \omega} \right] \right|^2 \times \delta(\omega - \omega_s - \omega_{fi}) \quad (5.21)$$

The summation over field modes may be expressed as an integral over frequencies by considering the density of field modes, ρ_k , in a cavity of volume V. Classically, ρ_k can be derived for a set of modes with each mode given by (k_x, k_y, k_z) . The result for the number of field modes between k and $k + dk$ for a single polarization is

$$\rho_k dk = \frac{k^2}{2\pi^2} dk \quad (5.22)$$

or with $k = \frac{\omega}{c}$

$$\rho_k dk = \rho_\omega d\omega = \frac{\omega^2}{2\pi^2 c^3} d\omega \quad (5.23)$$

The sum over the number of modes at ω_s , \sum_{k_s} for a volume, V, may then be replaced by an integration for a sufficiently large number of modes. With the integration over all possible solid angles, Ω , the summation becomes

$$\sum_{k_s} \rightarrow V \int \rho_{k_s} dk_s \int \frac{d\Omega}{4\pi} \rightarrow \frac{V}{(2\pi)^3} \int k_s^2 dk_s \int d\Omega \rightarrow \frac{V}{(2\pi)^3} \int \int \frac{\omega_s^2}{c^3} d\omega_s d\Omega \quad (5.24)$$

After substitution of $\frac{1}{\tau}$ from Eq (5.21) into Eq (5.1) and the use of

Eq (5.24), the Raman cross section is expressed as

$$\sigma = \frac{\omega}{f \ h^2 c^4} \int d\Omega \int d\omega_s \ \omega_s^3 \left| \sum_b \left[\left(\frac{d_{fb}^{\alpha_1} d_{bi}^{\alpha_2}}{\omega_{bi} + \omega_s} + \frac{d_{fb}^{\alpha_2} d_{bi}^{\alpha_1}}{\omega_{bi} - \omega_s} \right) a^{\alpha_1} a_s^{*\alpha_2} \right] \right|^2 \times \delta(\omega - \omega_s - \omega_{fi}) \quad (5.25)$$

In actuality, the delta function representing the density of states should be a generalized line shape which occurs when the energy levels involved are not discrete levels but have a probability distribution about a given level. Examples are:

(i) Lorentzian

$$g_L(\omega, \omega_s, \omega_{fi}) = \frac{1}{\pi} \frac{\Gamma}{[(\omega - \omega_{fi}) - \omega_s]^2 + \Gamma^2} \quad (5.26)$$

(ii) Gaussian

$$g_G(\omega, \omega_s, \omega_{fi}) = \frac{1}{\sqrt{2\pi} \delta} e^{-[(\omega - \omega_{fi}) - \omega_s]^2 / 2\delta^2} \quad (5.27)$$

$$\delta = \frac{\Gamma}{(2 \ln 2)}^{1/2} \quad (5.28)$$

where

$$\int g(\omega, \omega_s, \omega_{fi}) d\omega = 1 \quad (5.29)$$

If the variation of the integrand in Eq (5.25) can be neglected across the function $g(\omega, \omega_s, \omega_{fi})$ which is reasonable when no resonances occur, then the general differential cross section is

$$\left(\frac{d\sigma}{d\Omega}\right)_i = \sum_f \frac{(\omega_{fi} < \omega)}{\omega(\omega - \omega_{fi})^3} \left| \frac{1}{c^4} \sum_b \left[\left(\frac{d_{fb}^{a_1} d_{bi}^{a_2}}{\omega_{bf} + \omega} + \frac{d_{fb}^{a_2} d_{bi}^{a_1}}{\omega_{bi} - \omega} \right) a^{a_1} a_s^{*a_2} \right] \right|^2 \quad (5.30)$$

where the condition, $\omega_{fi} < \omega$, is necessary due to the conservation of energy for the delta function or the function representing a density of states. ω_{fi} defines the center of the scattered frequency line shape for

$$\omega_s = \omega - \omega_{fi} \quad (5.31)$$

Equation (5.30) represents the scattering of photons from the incident light beam due to all processes (Rayleigh and Raman) and for all possible states. The results obtained from this equation are slightly low because of the assumption of constant integrand made when integrating over the scattering frequency. But, the evaluation of the cross section exactly at the scattering frequency line center is acceptable. This approximation continues to hold even if a resonance occurs between ω and an electronic state of the molecule. In this case, the damping term, ignored in the energy states of molecule, must be considered. When this damping is taken into account (Ref 90:205)

$\left(\frac{d\sigma}{d\Omega}\right)_i$ is

$$\left(\frac{d\sigma}{d\Omega}\right)_i = \sum_f \frac{(\omega_{fi} < \omega)}{\omega(\omega - \omega_{fi})^3} \left| \frac{1}{c^4} \sum_b \left[\left(\frac{d_{fb}^{a_1} d_{bi}^{a_2}}{\omega_{bf} + \omega + i\Gamma_b} + \frac{d_{fb}^{a_2} d_{bi}^{a_1}}{\omega_{bi} - \omega - i\Gamma_b} \right) a^{a_1} a_s^{*a_2} \right] \right|^2 \quad (5.32)$$

In this work as in many applications, it is not the total scattering cross section that is needed but a differential cross section

associated with a specific final state, f . Thus a differential scattering cross section for each allowed final state, given the initial state, is defined. The allowed final states are those determined by the appropriate selection rules for the molecule (Ref 83:110).

The case $f=i$ in the summation of Eq (5.30) represents the Rayleigh differential scattering cross section. All of the other allowed final states represent Raman scattering. Thus, removing $f=i$ from the sum and defining a cross section for a given final state, $(\frac{d\sigma}{d\Omega})_{fi}$ as

$$(\frac{d\sigma}{d\Omega})_{fi} = \frac{\omega(\omega-\omega_f)^3}{c^4} \left| \frac{1}{\hbar} \sum_b \left[\frac{a_1 a_2}{\frac{d_{fb}}{\omega_{bf}+\omega} d_{bi}} + \frac{d_{fb} d_{bi}}{\omega_{bi}-\omega} \right] a^{\alpha_1} a_s^{*\alpha_2} \right|^2 \quad (5.33)$$

the cross section for scattering from a single initial state to a given final state is obtained. In this definition of the Raman differential cross section ω_{fi} may be positive or negative corresponding to Stokes or anti-Stokes scattering, respectively.

This expression for the differential cross section may be written in a form using the Raman polarizability tensor when the definition

$$\left[p_{\alpha_2 \alpha_1}^\omega \right]_{fi} = \frac{1}{\hbar} \sum_b \left[\frac{d_{fb} d_{bi}}{\omega_{bf}+\omega} + \frac{d_{fb} d_{bi}}{\omega_{bi}-\omega} \right] \quad (5.34)$$

is used. In this case $(\frac{d\sigma}{d\Omega})_{fi}$ becomes

$$(\frac{d\sigma}{d\Omega})_{fi} = \frac{\omega(\omega-\omega_f)^3}{c^4} \left| p_{\alpha_2 \alpha_1}^\omega a^{\alpha_1} a_s^{*\alpha_2} \right|^2 \quad (5.35)$$

where

$$\left| p_{\alpha_2 \alpha_1}^{\omega} a^{\alpha_1} a_s^{*\alpha_2} \right|^2 = p_{\alpha_2 \alpha_1} a^{\alpha_1} a_s^{*\alpha_2} p_{\alpha_4 \alpha_3} a^{*\alpha_3} a_s^{\alpha_4} \quad (5.36)$$

It will be shown later that this form is particularly useful when performing the orientational averaging.

General Comments

The cross section used in Eq (5.1) is the photon cross section. It is defined as the rate at which photons are removed from an incident beam in the scattering process divided by the rate of photons per unit area incident on a plane perpendicular to the direction of propagation. The scattering cross section at a frequency ω_s is

$$\sigma = \frac{\int n_s r^2 d\Omega}{n} \quad (5.37)$$

where r is the distance from the scattering center to the unit solid angle. The differential scattering cross section is

$$(\frac{d\sigma}{d\Omega})_n = \frac{n_s}{n} r^2 \quad (5.38)$$

From this equation, the number of photons scattered into the solid angle is

$$n_s = n (\frac{d\sigma}{d\Omega})_n r^{-2} \quad (5.39)$$

But the intensity (W/cm^2) is given by

$$I = n \hbar \omega c \quad (5.40)$$

and

$$n = \frac{I}{\hbar \omega c} \quad (5.41)$$

For Eq (5.41) substituted into Eq (5.39) and division of similar terms, an equation for the scattered intensity is

$$\frac{I_s}{\omega_s} = \frac{I}{\omega} \left(\frac{d\sigma}{d\Omega} \right)_n r^{-2} \quad (5.42)$$

or

$$I_s = I \frac{\omega_s}{\omega} \left(\frac{d\sigma}{d\Omega} \right)_n r^{-2} \quad (5.43)$$

A differential scattering cross section for intensity can then be defined as

$$\left(\frac{d\sigma}{d\Omega} \right) = \frac{\omega_s}{\omega} \left(\frac{d\sigma}{d\Omega} \right)_n \quad (5.44)$$

so that

$$I_s = I \left(\frac{d\sigma}{d\Omega} \right) r^{-2} \quad (5.45)$$

The intensity differential scattering cross section using $\left(\frac{d\sigma}{d\Omega} \right)_{fi}$ as given in Eq (5.35) with $\omega_s = (\omega - \omega_{fi})$ is

$$\left(\frac{d\sigma}{d\Omega} \right)_{fi} = \frac{\omega_s^4}{c^4} \left| \begin{matrix} \omega & a^{\alpha_1} & a^{*\alpha_2} \\ p_{\alpha_2 \alpha_1} & a_s & \end{matrix} \right|^2 \quad (5.46)$$

It is this differential scattering cross section that will be used in the remainder of this work. The cross section given by Eq (5.46) is also called the power cross section.

Another consideration that must be given to the use of cross sections available in the literature is that many cross section measurements are for an entire rotational band. In many experiments the

resolution of the system may be sufficient to resolve well separated branches (e.g., O, P, Q, R, S) but not individual rotational lines. In these situations, any cross section obtained is not for a single transition but for a sum over all populated states in the branch. Since the specification of the branch will determine the final state given the initial state (e.g., vibrational-rotational Q branch: [v,J] → [v+1, J]), the branch cross section is a sum of the individual cross sections over all possible initial states. The individual states must be weighted by a state density, ρ_{ii}^0 . The differential cross section for a branch is then given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{Br} = \sum_{i'} \rho_{ii'}^0 \left(\frac{d\sigma}{d\Omega}\right)_{fi} \quad (5.47)$$

where i' represents the initial states of the branch and $\left(\frac{d\sigma}{d\Omega}\right)_{fi}$ is from Eq (5.46). It is not possible in this situation to determine the individual differential cross sections from branch cross sections. However, a first approximation is to assume that all individual differential cross sections are equal

$$\left(\frac{d\sigma}{d\Omega}\right)_{fi'} = \left(\frac{d\sigma}{d\Omega}\right) \quad (5.48)$$

and may be removed from the summation so that

$$\left(\frac{d\sigma}{d\Omega}\right)_{Br} = \sum_{i'} \frac{N_{i'}}{N_{Br}} \left(\frac{d\sigma}{d\Omega}\right) \quad (5.49)$$

where $N_{i'}$ is the number of initial states. Then the individual differential cross section is approximated by

$$\left(\frac{d\sigma}{d\Omega}\right) = \left(\frac{d\sigma}{d\Omega}\right)_{Br} \quad (5.50)$$

This result weights the cross section to that of the most populated initial state.

Because the differential scattering cross section derived here is for an individual molecule, the elements of the polarizability tensor are in a molecule fixed coordinate system. It will be desirable to transform to a laboratory coordinate system in which measurements are made by a rotation of the axes. When this is performed, the elements may change value. However, for the general case of an unsymmetric tensor discussed in Chapter IV, the polarizability invariants a , γ^2 and δ^2 (Eq (4.81), (4.82) and (4.83)) are very useful. It will be shown that under orientational averaging, the differential scattering cross section can be expressed in terms of these invariants.

The dependence of the molecular differential scattering cross section on the vibrational quantum number, v , can be specified without regard to orientation. This dependence has been determined for the polarizability tensor elements from the expectation values (Ref 17:105 and Ref 83:78) following the approach of Placzek (Ref 76). These results will be used here to scale the polarizability and hence the differential cross section between any two vibrational states. In this approach, it is assumed that the Born-Oppenheimer approximation holds to decouple the electronic, vibrational and rotational motion. It is also assumed that the vibrational motion is in normal modes which do not couple with each other. Thus the manifold of vibrational quantum numbers, $[v]$, may be held fixed with the exception of those describing the particular transitions taking place. Under these assumptions, the desired scaling is obtained in terms of the vibrational quantum number of the initial state, the polarizability tensor

elements for transition from ground vibrational state $[p_{\alpha\beta}]_0$ (e.g., for $\Delta v = +1$, $[p_{\alpha\beta}]_0 = [p_{\alpha\beta}]_{10}$), and the ratio of the ground vibrational state energy to that of the vibrational state of interest, $\tilde{\nu}_v$. For example, when $\Delta v = +1$

$$[p_{\alpha\beta}]_{v+1,v} = (v+1)^{1/2} (\tilde{\nu}_0 / \tilde{\nu}_v)^{1/2} [p_{\alpha\beta}]_0 \quad (5.51)$$

where $\tilde{\nu}_v$ is the energy of the initial vibration state in wavenumbers. This energy ratio is to a first order not dependent on the vibrational quantum number. As an example, consider the vibrational energy level of a diatomic molecule when anhromonicity has been included. This vibrational energy may be written as (Ref 91:92)

$$\frac{E_v}{hc} = G(v) = \nu_e (v+1/2) - \nu_e x_e (v+1/2)^2 + \nu_e y_e (v+1/2)^3 + \dots \quad (5.52)$$

$$\text{where } \nu_e \gg \nu_e x_e \gg \nu_e y_e \gg \dots \quad (5.53)$$

Defining $\tilde{\nu}_v$ as

$$\tilde{\nu}_v = \frac{E_v}{(v+1/2)hc} = \frac{G(v)}{(v+1/2)} \quad (5.54)$$

similar to the harmonic oscillator. From Eq (5.52)

$$\tilde{\nu}_v = \nu_e - \nu_e x_e (v+1/2) + \nu_e y_e (v+1/2)^2 + \dots \quad (5.55)$$

From this equation and the inequalities of Eq (5.53), $\tilde{\nu}_v$ is to a first order independent of v . $[p_{\alpha\beta}]_{fi}$ for $\Delta v = +1$ then scales as $(v+1)^{1/2}$. Upon substitution of Eq (5.51) into Eq (5.46) the desired scaling for the differential cross section is

$$\text{or } \left(\frac{d\sigma}{d\Omega} \right)_{v+1,v} = \frac{\omega_s^4}{c^4} (v+1) \left(\frac{\nu_0}{\nu_v} \right) \left| [p_{\alpha_2 \alpha_1}^\omega]_0 a^{\alpha_1} a^{*\alpha_2} s \right|^2 \quad (5.56)$$

$$\left(\frac{d\sigma}{d\Omega} \right)_{v+1,v} = (v+1) \left(\frac{\nu_0}{\nu_v} \right) \left(\frac{d\sigma}{d\Omega} \right)_0 \quad (5.57)$$

when $\Delta v = +1$. Table VI, following Long (Ref 83), gives the polarizability and differential cross sections for several different transitions. This result is consistent with that of Eq (3.47) when the energy difference between vibrational states is negligible.

TABLE VI Vibrational Scaling of the Raman
Polarizability Tensor Elements and Differential Cross Section

| Selection Rule, Δv | Initial State, f | Final State, f | $[p_{\alpha\beta}]_{fi} / [p_{\alpha\beta}]_0$ | $(d\sigma/d\Omega)_{fi} / (d\sigma/d\Omega)_0$ |
|----------------------------|--------------------|-------------------------|---|--|
| 0 | $[v]$ | $[v]$ | 1 | 1 |
| +1 | $[v], v$ | $[v], v+1$ | $[(v+1)(\tilde{v}_0/\tilde{v}_v)]^{1/2}$ | $(v+1)(\tilde{v}_0/\tilde{v}_v)$ |
| -1 | $[v], v$ | $[v], v-1$ | $[(v)(\tilde{v}_0/\tilde{v}_v)]^{1/2}$ | $v(\tilde{v}_0/\tilde{v}_v)$ |
| +2 | $[v], v$ | $[v], v+2$ | $[\frac{1}{2}(v+1)(v+2)]^{\frac{1}{2}}(\tilde{v}_0/\tilde{v}_v)$ | $\frac{1}{2}(v+1)(v+2)(\tilde{v}_0/\tilde{v}_v)^2$ |
| -2 | $[v], v$ | $[v], v-2$ | $[\frac{1}{2}(v-1)v]^{\frac{1}{2}}(\tilde{v}_0/\tilde{v}_v)$ | $\frac{1}{2}(v-1)v(\tilde{v}_0/\tilde{v}_v)^2$ |
| +1, +1 | $[v], v_1, v_m$ | $[v], v_1+1$ v_m+1 | $\left[\frac{(\tilde{v}_1 \tilde{v}_m)_0}{(v_1+1)(v_m+1) (\frac{(v_1 v_m)_0}{(v_1 v_m)_v})} \right]^{\frac{1}{2}}$ | $(v_1+1)(v_m+1) \frac{(\tilde{v}_1 \tilde{v}_m)_0}{(\tilde{v}_1 \tilde{v}_m)_v}$ |
| -1, -1 | $[v], v_1, v_m$ | $[v], v_1-1$ v_m-1 | $\left[\frac{(\tilde{v}_1 \tilde{v}_m)_0}{v_1 v_m (\frac{(v_1 v_m)_0}{(v_1 v_m)_v})} \right]^{\frac{1}{2}}$ | $v_1 v_m \frac{(\tilde{v}_1 \tilde{v}_m)_0}{(\tilde{v}_1 \tilde{v}_m)_v}$ |

[†] $[v]$ represents the manifold of vibrational states not participating in the transition.

VI Orientational Averaging

Quantum Number and Coordinate Dependence

As pointed out in Chapter III, the interpretation of CARS data as well as that for the other third order processes depends on having macroscopic equations for the response of a medium. Since the macroscopic response results from the contribution of many molecules even in a dilute gas, it is necessary to take the correct average of the molecular dipole moments, Eq (3.7). This average depends upon the orientation of the molecules. For a molecular gas, being considered here, this orientation is determined by specifying the coordinate system (i.e., laboratory or molecular) and the quantum state of the molecule. The coordinate system may be chosen arbitrarily but should be one that simplifies computations. Once the coordinate system is selected, the specification of a complete set of quantum numbers determines the orientation of the molecule and the statistical distribution in the coordinate system. In this chapter the effect of orientational averaging is determined with many of the details in Appendices H and I. The results are applied to a generic dipole moment expectation value characteristic of those in Chapter IV and to the molecular differential scattering cross section of Chapter V.

The complete set of quantum numbers required for a molecular gas are those for electronic, vibration, total angular momentum, nature of momentum coupling (e.g., angular momentum about the internuclear axis), and a component of the angular momentum (e.g., in the direction of a perturbing magnetic field) denoted by ($n, v, J, N(K), M$). The averages obtained are also a function of this set of quantum numbers

and the labeling of spectral lines must be done by changes in each of the numbers. Such quantities as the susceptibilities, scattering cross sections and the invariants a , γ and δ would depend on the initial state. Their values could vary for each line in the spectrum. To uniquely determine this set of quantum numbers, it is, however, necessary to have a weak perturbing magnetic field present. Otherwise, the energy levels associated with the values of M for a given J are $2J+1$ -fold degenerate. For the conditions being treated here, this perturbing field is not present and the set of quantum numbers are restricted to $(n, v, J, N (K))$. In this situation, it is not possible to determine the contribution of M .

The molecules of a gas specified by this reduced set of quantum numbers have a random orientation. This can be seen for a diatomic molecule by summing the probability of finding the molecule in a given orientation (Ref 91:69) and dividing by $2J+1$. The result is $1/4\pi$ which is isotropic and independent of J . The result from orientational averaging for molecules specified by (n, v, J, N) are also dependent on the same quantum numbers. To determine these averages from experimental data, the spectral data must be identified by both the initial quantum numbers and the change in those numbers. It is to be expected that such quantities as the invariants a, γ , and δ will vary from spectral line to line and scale with the given set of quantum numbers. This scaling of the polarizability and the differential scattering cross section with v , independent of the average, was given in Chapter V. Placzek and Teller (Ref 76: Table 2) give the scaling of the polarizability tensor elements with J in a similar manner and

this result will be presented in this chapter without further proof. Because of the dependence on specification of the quantum numbers, care must be taken in using experimental results from the literature. For example, values of the polarizability invariants α' , γ' and δ' are different when determined from a measurement using a branch where the quantum number set has been reduced to (n, v) than those for either individually resolved rotational spectra or vibrational-rotational spectra. Similarly, calculations made for a given set of quantum numbers must be so specified.

With this understanding of the role of the quantum number set, a careful consideration of the coordinate system selection must be made before obtaining the necessary averages. Since measurements are made in a laboratory coordinate system, L , it is reasonable to want the final macroscopic equations to be expressed in this system where the electric fields are specified. But the polarizabilities which are important in the calculation of the molecular dipole moments are a response to the applied field and as such depend upon the field direction but not the magnitude. Because of the random orientation of the molecules in an unperturbed gas, these polarizabilities would be different for each molecule. It is, therefore, easier to calculate the molecular polarizabilities in a coordinate system attached to the molecule itself. This molecular coordinate system, I , could be one that diagonalizes the Rayleigh polarization tensor thus corresponding to the principal axes of the Rayleigh polarizability ellipsoid, or a momental system which diagonalizes the moment of inertia. The exact character of the molecular coordinate system is not important here, what is important is that it be the same for each molecule. Under

this condition, the molecular equations derived in previous chapters apply and the expressions are the same for each identical molecule.

Based on the above comments, it is desirable to obtain the third order polarization, $\bar{P}^{(3)}$, for use in the Maxwell's equations, in a laboratory coordinate system. However, the polarizabilities are best obtained in a molecular coordinate system where they are constants independent of the averaging process. This is possible by transforming from one coordinate system to the other using rotation through the Euler angles ϕ , θ and ψ . These rotation transformations are $R_1(\phi)$, $R_2(\theta)$ and $R_3(\psi)$. Appendix H gives the definition and use of the rotations.

Susceptibilities

The polarization of a gas was defined by Eq (3.7) in terms of the average dipole moment. Equations (4.45), (4.46), (4.47), and (4.48) give an expression for the dipole moments induced at different electric field frequencies. These dipole moments are made up of components that arise from the different third order processes and have the general component form

$$\langle \bar{d}_i^{(3)} \rangle = C_i \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \bar{P}_i^{(3)} (-\omega; \omega', \omega'', \omega''') \hat{a}_1^* \hat{a}_2 \hat{a}_3 \\ \times \epsilon_1^*(-\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \quad (6.1)$$

which may be written in component form as

$$\langle d_\mu^i \rangle = C_i \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' P_{\mu \alpha_1 \alpha_2 \alpha_3}^i (-\omega; \omega', \omega'', \omega''') a_1^{*\alpha_1} a_2^{\alpha_2} a_3^{\alpha_3} \\ \times \epsilon_1^*(-\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \quad (6.2)$$

where C_i is the correct numerical factor. Since the average of a sum is the sum of the averages, the required orientational averaging can be performed on a general term as expressed in Eq (6.2). The results of this averaging are then applied to the specific form of polarizabilities given in Appendix G and the related electric field elements for the sixteen $\langle \bar{d}^i \rangle$ of Chapter IV. The result will also be applied to the Raman differential scattering cross section of Chapter V.

To perform the averaging for a gas, it is assumed that there is a large enough ensemble of a particular molecule so that all orientations are possible and they are randomly distributed. As was discussed in the first section of this chapter, for an unperturbed gas, this is a good assumption. It is also assumed that the ensemble of the particular M molecules have the properties:

- (1) The molecules are distinguishable to allow the use of Maxwell-Boltzmann statistics.
- (2) The molecules are independent. This requires the gas to be dilute enough so that there is no interaction between molecules.
- (3) The molecules are identical. This precludes the need to discriminate between overlapping spectral lines.
- (4) Only the induced dipole moments contribute. The molecule is assumed to be too massive to move under the influence of a high frequency (visible frequencies) field so that any permanent dipole moment is also random and averages to zero.

For a system of discrete entities, the average is defined by

$$\bar{C} = \frac{\sum_{m=1}^M C_m}{M} \quad (6.3)$$

The average dipole moment is then

$$\overline{\langle d_u^i \rangle}^{(\tau)} = \frac{1}{M} \sum_{m=1}^M \langle d_u^i \rangle_m \quad (6.4)$$

where

$$\langle d_u^i \rangle_m = (R^T)_u^m \langle d_u^i \rangle_m \quad (6.5)$$

$(R^T)_u^m$ is the transpose of R_u^m given in Appendix H and $(R^T)_u^m = R_u^m$.

Upon substitution of Eq (6.2) and ignoring the factor C_i

$$\overline{\langle d_u^i \rangle} = \frac{1}{M} \sum_{m=1}^M \left[R_u^m \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' p_{\mu\alpha_1\alpha_2\alpha_3}^i (-\omega; \omega', \omega'', \omega''') \right. \\ \left. \times \epsilon_1^{*\alpha_1}(-\omega') \epsilon_2^{\alpha_2}(\omega'') \epsilon_3^{\alpha_3}(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \right]_m \quad (6.6)$$

where $\epsilon^\alpha = a^\alpha \epsilon$ has been used for convenience. It is possible to interchange the integral and summation with the result

$$\overline{\langle d_u^i \rangle} = \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \frac{1}{M} \sum_{m=1}^M \left[R_u^m p_{\mu\alpha_1\alpha_2\alpha_3}^i (-\omega; \omega', \omega'', \omega''') \right. \\ \left. \times \epsilon_1^{*\alpha_1}(-\omega') \epsilon_2^{\alpha_2}(\omega'') \epsilon_3^{\alpha_3}(\omega''') \right]_m \delta(\omega - \omega' - \omega'' - \omega''') \quad (6.7)$$

In this form, the dipole moment for each molecule would need to be computed and summed. This would be an impossible task for any gas of

interest. By rotation through a set of Euler angles (Appendix H), a transformation of ϵ from the molecular coordinate system to the laboratory coordinate system simplifies the averaging. From Eq (H14)

$$\epsilon_i^a = R_\alpha^a \epsilon_i^a$$

where the same symbols are used as in Appendix H for R elements.

Equation (6.7) can then be written as

$$\overline{\langle d_u^i \rangle} = \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \frac{1}{M} \sum_{m=1}^M \left[R_\mu^u p_{\mu\alpha_1\alpha_2\alpha_3}^i (-\omega; \omega', \omega'', \omega''') \times R_{\alpha_1}^{a_1} \epsilon^{*a_1}(-\omega') R_{\alpha_2}^{a_2} \epsilon^{a_2}(\omega'') R_{\alpha_3}^{a_3} \epsilon^{a_3}(\omega''') \right]_m \delta(\omega - \omega' - \omega'' - \omega''') \quad (6.8)$$

But the fields ϵ_i^a are in laboratory coordinates and do not vary from molecule to molecule. They may therefore be removed from the summation. Also $[p_{\mu\alpha_1\alpha_2\alpha_3}^i]_m$ is in an identical fixed molecular coordinate system for each molecule so that

$$[p_{\mu\alpha_1\alpha_2\alpha_3}^i]_1 = [p_{\mu\alpha_1\alpha_2\alpha_3}^i]_2 = \dots = [p_{\mu\alpha_1\alpha_2\alpha_3}^i]_m = p_{\mu\alpha_1\alpha_2\alpha_3}^i \quad (6.9)$$

and may also be taken out of the sum. With these changes, Eq (6.8) becomes

$$\overline{\langle d_u^i \rangle} = \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \sum_{m=1}^M \frac{1}{M} [R_\mu^u R_{\alpha_1}^{a_1} R_{\alpha_2}^{a_2} R_{\alpha_3}^{a_3}]_m p_{\mu\alpha_1\alpha_2\alpha_3}^i (-\omega; \omega', \omega'', \omega''') \times \epsilon_1^{*a_1}(-\omega') \epsilon_2^{a_2}(\omega'') \epsilon_3^{a_3}(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \quad (6.10)$$

It is now only necessary to perform the sum of the rotation matrices to obtain the average dipole moment of the gas. But this is still an impossible task for M molecules. However, because M is very large, an

excellent approximation can be made to obtain the average. For a large M the definition of average given by Eq (6.3) may be replaced by

$$\bar{C} = \frac{\int f(\tau) C_m(\tau) d\tau}{\int f(\tau) d\tau} \quad (6.11)$$

where $f(\tau)$ = distribution function

τ = complete coordinate set.

For a random orientation $f(\tau)$ becomes

$$f(\theta, \phi, \psi) = \sin \theta \quad (6.12)$$

After applying Eq (6.11) to $[R_{\mu}^U R_{\alpha_1}^{\alpha_1} R_{\alpha_2}^{\alpha_2} R_{\alpha_3}^{\alpha_3}]$ with this definition of $f(\theta, \phi, \psi)$, the following result is obtained (Appendix I)

$$\begin{aligned} [R_{\mu}^U R_{\alpha_1}^{\alpha_1} R_{\alpha_2}^{\alpha_2} R_{\alpha_3}^{\alpha_3}] &= \frac{1}{30} [(4 \delta_{\mu\alpha_2}^{\alpha_1\alpha_3} - \delta_{\mu\alpha_1}^{\alpha_2\alpha_3} - \delta_{\mu\alpha_3}^{\alpha_1\alpha_2}) \delta_{\alpha_1}^U \delta_{\alpha_3}^{\alpha_2} \\ &\quad - (\delta_{\mu\alpha_2}^{\alpha_1\alpha_3} - 4 \delta_{\mu\alpha_1}^{\alpha_2\alpha_3} + \delta_{\mu\alpha_1}^{\alpha_3\alpha_2}) \delta_{\alpha_2}^U \delta_{\alpha_3}^{\alpha_1} \\ &\quad - (\delta_{\mu\alpha_2}^{\alpha_1\alpha_3} + \delta_{\mu\alpha_1}^{\alpha_2\alpha_3} - 4 \delta_{\mu\alpha_1}^{\alpha_3\alpha_2}) \delta_{\alpha_3}^U \delta_{\alpha_2}^{\alpha_1}] \quad (6.13) \end{aligned}$$

where

$$\delta_{\mu\alpha_2}^{\alpha_1\alpha_3} \equiv \delta_{\mu}^{\alpha_1} \delta_{\alpha_2}^{\alpha_3} \quad (6.14)$$

The application of Eq (6.14) to the polarizabilities obtained in Chapter IV, $p_{\mu\alpha_1\alpha_2\alpha_3}^i$, produces

$$\delta_{\mu}^{\alpha_1} \delta_{\alpha_2}^{\alpha_3} p_{\mu\alpha_1\alpha_2\alpha_3}^i = \delta_{\mu}^{\alpha_1} p_{\mu\alpha_1\alpha_3\alpha_3}^i = p_{\alpha_1\alpha_1\alpha_3\alpha_3}^i \quad (6.15)$$

From the definition of the Einstein convention

$$p_{\alpha_1 \alpha_1 \alpha_3 \alpha_3}^i = p_{1111}^i + p_{1122}^i + p_{1133}^i + \dots + p_{3322}^i + p_{3333}^i \quad (6.16)$$

The application of $\delta_{a_1}^u$ to ϵ_1^a is given by

$$\delta_{a_1}^u \epsilon_1^a = \epsilon_1^u \quad (6.17)$$

The use of Eq (6.13) in Eq (6.10) then gives the following result for the average dipole moment in the laboratory coordinate system

$$\begin{aligned} \overline{\langle d_u^i \rangle} &= \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \frac{1}{30} \left\{ [4p_{\mu\mu\alpha\alpha}^i - p_{\mu\alpha\mu\alpha}^i - p_{\mu\alpha\alpha\mu}^i] \epsilon_1^{*u} \epsilon_2^a \epsilon_3^a \right. \\ &\quad - [p_{\mu\mu\alpha\alpha}^i - 4p_{\mu\alpha\mu\alpha}^i + p_{\mu\alpha\alpha\mu}^i] \epsilon_1^{*a} \epsilon_2^u \epsilon_3^a \\ &\quad \left. - [p_{\mu\mu\alpha\alpha}^i + p_{\mu\alpha\mu\alpha}^i - 4p_{\mu\alpha\alpha\mu}^i] \epsilon_1^{*a} \epsilon_2^a \epsilon_3^u \right\} \\ &\quad \times \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (6.18)$$

where the frequency dependence of p^i and ϵ^a has been suppressed for convenience. The indices have also been reduced to μ , α , u and a since they are now a dummy set indicating a sum. Equation (6.18) can be written in a vector form which shows more clearly the vector nature of the average dipole moment. Written in this form, the average dipole moment when substituted into Eq (3.7) produces the nonlinear polarization for each of the processes. In generalized form, this is

$$\begin{aligned} \bar{P}^i(\omega) = \frac{N}{30} \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \left\{ A(-\omega; \omega', \omega'', \omega''') [\bar{\epsilon}_2(\omega') \cdot \bar{\epsilon}_3(\omega'')] \bar{\epsilon}_1^*(-\omega') \right. \\ - B(-\omega; \omega', \omega'', \omega''') [\bar{\epsilon}_1^*(-\omega') \cdot \bar{\epsilon}_3(\omega'')] \bar{\epsilon}_2(\omega'') \\ \left. - C(-\omega; \omega', \omega'', \omega''') [\bar{\epsilon}_1^*(-\omega') \cdot \bar{\epsilon}_2(\omega'')] \bar{\epsilon}_3(\omega''') \right\} \\ \times \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (6.19)$$

where

$$A(-\omega; \omega', \omega'', \omega''') = \quad (6.20)$$

$$4p_{\mu\mu\alpha\alpha}^i(-\omega; \omega', \omega'', \omega''') - p_{\mu\alpha\mu\alpha}^i(-\omega; \omega', \omega'', \omega''') - p_{\mu\alpha\alpha\mu}^i(-\omega; \omega', \omega'', \omega''')$$

$$B(-\omega; \omega', \omega'', \omega''') = \quad (6.21)$$

$$p_{\mu\mu\alpha\alpha}^i(-\omega; \omega', \omega'', \omega''') - 4p_{\mu\alpha\mu\alpha}^i(-\omega; \omega', \omega'', \omega''') + p_{\mu\alpha\alpha\mu}^i(-\omega; \omega', \omega'', \omega''')$$

$$C(-\omega; \omega', \omega'', \omega''') = \quad (6.22)$$

$$p_{\mu\mu\alpha\alpha}^i(-\omega; \omega', \omega'', \omega''') + p_{\mu\alpha\mu\alpha}^i(-\omega; \omega', \omega'', \omega''') - 4p_{\mu\alpha\alpha\mu}^i(-\omega; \omega', \omega'', \omega''')$$

The susceptibility tensor elements may be determined for a specific process i from Eq (6.19). The isotropic conditions given in Chapter IV, Eq (4.92), are shown to hold for the result of Eq (6.19). The integrand in Eq (6.19), may be written as

$$\begin{aligned} I_u = & A (\epsilon_2^1 \epsilon_3^1 + \epsilon_2^2 \epsilon_3^2 + \epsilon_2^3 \epsilon_3^3) \epsilon_1^* u - B (\epsilon_1^{*1} \epsilon_3^1 + \epsilon_1^{*2} \epsilon_3^2 + \epsilon_1^{*3} \epsilon_3^3) \epsilon_2 u \\ & - C (\epsilon_1^{*1} \epsilon_2^1 + \epsilon_1^{*2} \epsilon_2^2 + \epsilon_1^{*3} \epsilon_2^3) \epsilon_3 u \end{aligned} \quad (6.23)$$

where the frequency dependence of A , B , C and ϵ_i^* has been suppressed for convenience. Upon expansion, Eq (6.23) becomes

$$\begin{aligned}
 I_u = & A \epsilon_1^{*u} \epsilon_2^1 \epsilon_3^1 - B \epsilon_1^{*1} \epsilon_2^u \epsilon_3^1 - C \epsilon_1^{*1} \epsilon_2^1 \epsilon_3^u \\
 & + A \epsilon_1^{*u} \epsilon_2^2 \epsilon_3^2 - B \epsilon_1^{*2} \epsilon_2^u \epsilon_3^2 - C \epsilon_1^{*2} \epsilon_2^2 \epsilon_3^u \\
 & + A \epsilon_1^{*u} \epsilon_2^3 \epsilon_3^3 - B \epsilon_1^{*3} \epsilon_2^u \epsilon_3^3 - C \epsilon_1^{*3} \epsilon_2^3 \epsilon_3^u
 \end{aligned} \tag{6.24}$$

Noting that

$$\frac{30}{N} I_u = x'_{uabc} \epsilon_1^{*a} \epsilon_2^b \epsilon_3^c \tag{6.25}$$

the expressions for x'_{uabc}^i can be written from Eq (6.24) as

$$x'_{1111} = A - B - C \tag{i}$$

$$x'_{2222} = A - B - C \tag{ii}$$

$$x'_{3333} = A - B - C \tag{iii} \tag{6.26}$$

The isotropic condition $x_{1111} = x_{2222} = x_{3333}$ is seen to apply.

Continuing the determination of x' from Eq (6.24)

$$x'_{1122} = A = x'_{1133} = x'_{2211} = x'_{2233} = x'_{3311} = x'_{3322} \tag{6.27}$$

$$x'_{1212} = -B = x'_{1313} = x'_{2121} = x'_{2323} = x'_{3131} = x'_{3232} \tag{6.28}$$

$$x'_{1221} = -C = x'_{1331} = x'_{2112} = x'_{2332} = x'_{3113} = x'_{3223} \tag{6.29}$$

All other susceptibility tensor elements must be zero since the fields $\bar{\epsilon}_1^*$, $\bar{\epsilon}_2$ and $\bar{\epsilon}_3$ are arbitrary so there is no restriction on their components. This result with those of Eqs (6.27), (6.28) and (6.29) meet the conditions for an isotropic medium. The final isotropic condition of Eq (4.92)

$$x_{1111}^i = x_{1122}^i + x_{1212}^i + x_{1221}^i$$

can also be seen to hold. The result of Eq (6.19) is therefore applicable to a gas which is isotropic and the orientational averaging performed was correct.

Equations (6.20), (6.21) and (6.22) when substituted into Eqs (6.26) (6.27), (6.28) and (6.29) give the form of the susceptibility tensor elements.

$$\begin{aligned} x_{1111}^i(-\omega; \omega', \omega'', \omega''') &= \frac{N}{15} [p_{\mu\mu\alpha\alpha}^i(-\omega; \omega', \omega'', \omega''') + p_{\mu\alpha\mu\alpha}^i(-\omega; \omega', \omega'', \omega''')] \\ &\quad + p_{\mu\alpha\alpha\mu}^i(-\omega; \omega', \omega'', \omega''')] \end{aligned} \quad (6.30)$$

$$\begin{aligned} x_{1122}^i(-\omega; \omega', \omega'', \omega''') &= \frac{N}{30} [4p_{\mu\mu\alpha\alpha}^i(-\omega; \omega', \omega'', \omega''') - p_{\mu\alpha\mu\alpha}^i(-\omega; \omega', \omega'', \omega''')] \\ &\quad - p_{\mu\alpha\alpha\mu}^i(-\omega; \omega', \omega'', \omega''')] \end{aligned} \quad (6.31)$$

$$\begin{aligned} x_{1212}^i(-\omega; \omega', \omega'', \omega''') &= \frac{N}{30} [-p_{\mu\mu\alpha\alpha}^i(-\omega; \omega', \omega'', \omega''') + 4p_{\mu\alpha\mu\alpha}^i(-\omega; \omega', \omega'', \omega''')] \\ &\quad - p_{\mu\alpha\alpha\mu}^i(-\omega; \omega', \omega'', \omega''')] \end{aligned} \quad (6.32)$$

$$\begin{aligned} x_{1222}^i(-\omega; \omega', \omega'', \omega''') &= \frac{N}{30} [-p_{\mu\mu\alpha\alpha}^i(-\omega; \omega', \omega'', \omega''') - p_{\mu\alpha\mu\alpha}^i(-\omega; \omega', \omega'', \omega''')] \\ &\quad + 4p_{\mu\alpha\alpha\mu}^i(-\omega; \omega', \omega'', \omega''')] \end{aligned} \quad (6.33)$$

The polarization $\bar{P}^i(\omega)$ is then written as

$$\begin{aligned}
\bar{P}^i(\omega) = & \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \left\{ x_{1122}^i(-\omega; \omega', \omega'', \omega''') [\bar{\epsilon}_2(\omega'') \cdot \bar{\epsilon}_3(\omega''')] \bar{\epsilon}_1^*(-\omega') \right. \\
& + x_{1212}^i(-\omega; \omega', \omega'', \omega''') [\bar{\epsilon}_1^*(-\omega') \cdot \bar{\epsilon}_3(\omega''')] \bar{\epsilon}_2(\omega'') \\
& \left. + x_{1221}^i(-\omega; \omega', \omega'', \omega''') [\bar{\epsilon}_1^*(-\omega') \cdot \bar{\epsilon}_2(\omega'')] \bar{\epsilon}_3(\omega''') \right\} \\
& \times \delta(\omega - \omega' - \omega'' - \omega''')
\end{aligned} \tag{6.34}$$

Either Eq (6.34) or (6.19) must then be applied to the sixteen terms in Eqs (4.45) through (4.48).

Raman Cross Section

The Raman differential scattering cross section, $(\frac{d\sigma}{d\Omega})_{fi}$, given by Eq (5.46) was derived for an individual molecule. In order to use the result, it too must be averaged over all possible molecular orientations. This is carried out here in a method analogous to the preceding section. The assumptions given there are also applied here. The average differential cross section is

$$(\frac{d\sigma}{d\Omega})_{fi} = N \rho_{ii}^o \overline{(\frac{d\sigma}{d\Omega})_{fi}^m} \tag{6.35}$$

where $\overline{(\frac{d\sigma}{d\Omega})_{fi}^m}$ from Eq (5.47) is

$$(\frac{d\sigma}{d\Omega})_{fi}^m = \frac{\omega_s^4}{c^4} \left| p_{\alpha_2 \alpha_1}^{\omega} \xi_{s}^{\alpha_1} \xi_s^{*\alpha_2} \right|^2 \tag{6.36}$$

where the polarization vector is now written as ξ to avoid confusion. It is only the absolute quantity squared in this equation that must be averaged. From Eq (5.36)

$$\overline{|p_{\alpha_2 \alpha_1}^{\omega} \xi_s^{\alpha_1} \xi_s^{\alpha_2}|^2} = \overline{p_{\alpha_2 \alpha_1}^{\omega} \xi_s^{\alpha_1} \xi_s^{*\alpha_2} p_{\alpha_4 \alpha_3}^{*\omega} \xi_s^{*\alpha_3} \xi_s^{\alpha_4}} = \overline{|S_{if}|^2} \quad (6.37)$$

but the polarization vectors, $\hat{\xi}$, may be written in laboratory coordinates by a rotational transformation Eq (H14)

$$\xi^a = R_a^a \xi^a \quad (6.38)$$

Substitution of this into Eq (6.37) yields

$$\overline{|S_{if}|^2} = \overline{p_{\alpha_2 \alpha_1}^{\omega} R_{\alpha_1}^{\alpha_1} \xi_{\alpha_1}^{\alpha_1} R_{\alpha_2}^{\alpha_2} \xi_s^{*\alpha_2} p_{\alpha_4 \alpha_3}^{*\omega} R_{\alpha_3}^{\alpha_3} \xi_{\alpha_3}^{*\alpha_3} R_{\alpha_4}^{\alpha_4} \xi_s^{\alpha_4}} \quad (6.39)$$

Again, the Raman polarizability terms are constants determined in a molecular coordinate system and are independent of orientational averaging. Also, the polarization vectors are in a laboratory coordinate system and do not depend on the average. Equation (6.39) becomes

$$\overline{|S_{if}|^2} = \overline{R_{\alpha_1}^{\alpha_1} R_{\alpha_2}^{\alpha_2} R_{\alpha_3}^{\alpha_3} R_{\alpha_4}^{\alpha_4} p_{\alpha_2 \alpha_1}^{\omega} p_{\alpha_3 \alpha_4}^{*\omega} \xi_{\alpha_1}^{\alpha_1} \xi_s^{*\alpha_2} \xi_{\alpha_3}^{*\alpha_3} \xi_s^{\alpha_4}} \quad (6.40)$$

This average is the one obtained in Appendix I, Eq (I37) which upon application to Eq (6.40) yields

$$\begin{aligned}
\overline{|S_{if}|^2} = & \frac{1}{30} [\delta_{\alpha_1}^{\alpha_2} \delta_{\alpha_3}^{\alpha_4} (4 \delta_{\alpha_1}^{\alpha_2} \delta_{\alpha_3}^{\alpha_4} - \delta_{\alpha_1}^{\alpha_3} \delta_{\alpha_2}^{\alpha_4} - \delta_{\alpha_1}^{\alpha_4} \delta_{\alpha_2}^{\alpha_3}) \\
& + \delta_{\alpha_3}^{\alpha_1} \delta_{\alpha_4}^{\alpha_2} (-\delta_{\alpha_1}^{\alpha_2} \delta_{\alpha_3}^{\alpha_4} + 4 \delta_{\alpha_1}^{\alpha_3} \delta_{\alpha_2}^{\alpha_4} - \delta_{\alpha_1}^{\alpha_4} \delta_{\alpha_2}^{\alpha_3}) \\
& + \delta_{\alpha_4}^{\alpha_1} \delta_{\alpha_3}^{\alpha_2} (-\delta_{\alpha_1}^{\alpha_2} \delta_{\alpha_3}^{\alpha_4} - \delta_{\alpha_1}^{\alpha_3} \delta_{\alpha_2}^{\alpha_4} + 4 \delta_{\alpha_1}^{\alpha_4} \delta_{\alpha_2}^{\alpha_3})] \\
& \times p_{\alpha_2 \alpha_1}^{\omega} p_{\alpha_3 \alpha_4}^{*\omega} \xi_s^{\alpha_1} \xi_s^{*\alpha_2} \xi_s^{*\alpha_3} \xi_s^{\alpha_4} \quad (6.41)
\end{aligned}$$

$$\begin{aligned}
\overline{|S_{if}|^2} = & \frac{1}{30} [(4 p_{\alpha\alpha}^{\omega} p_{\beta\beta}^{*\omega} - p_{\alpha\beta}^{\omega} p_{\alpha\beta}^{*\omega} - p_{\alpha\beta}^{\omega} p_{\beta\alpha}^{*\omega}) \xi^{\alpha} \xi_s^{*\alpha} \xi^{\beta} \xi_s^{\beta} \\
& + (-p_{\alpha\alpha}^{\omega} p_{\beta\beta}^{*\omega} + 4 p_{\alpha\beta}^{\omega} p_{\alpha\beta}^{*\omega} - p_{\alpha\beta}^{\omega} p_{\beta\alpha}^{*\omega}) \xi^{\alpha} \xi_s^{*\alpha} \xi_s^{\beta} \xi_s^{*\beta} \\
& + (-p_{\alpha\alpha}^{\omega} p_{\beta\beta}^{*\omega} - p_{\alpha\beta}^{\omega} p_{\alpha\beta}^{*\omega} + 4 p_{\alpha\beta}^{\omega} p_{\beta\alpha}^{*\omega}) \xi^{\alpha} \xi_s^{\alpha} \xi^{\beta} \xi_s^{*\beta}] \quad (6.42)
\end{aligned}$$

where the repeated indices imply a sum (e.g., $p_{\alpha\alpha} = p_{11} + p_{22} + p_{33}$).

When these sums are expanded and compared to the invariants

a^2 , γ^2 and δ^2 of Eqs (4.81), (4.82) and (4.83), the terms in parenthesis are expressable as linear combinations of the polarizability invariants. As pointed out in the first section of this chapter, these rotational invariants are functions of the energy state (n , v , J).

$$p_{\alpha\alpha}^{\omega} p_{\beta\beta}^{*\omega} = 9 a^2 = A' \quad (6.43)$$

$$p_{\alpha\beta}^{\omega} p_{\alpha\beta}^{*\omega} = 3a^2 + \frac{2}{3} \gamma^2 + \frac{2}{3} \delta^2 = B' \quad (6.44)$$

$$p_{\alpha\beta}^{\omega} p_{\beta\alpha}^{*\omega} = 3a^2 + \frac{2}{3} \gamma^2 - \frac{2}{3} \delta^2 = C' \quad (6.45)$$

The terms in Eq (6.42) are then

$$4A' - B' - C' = 30a^2 - \frac{4}{3} \gamma^2 \quad (6.46)$$

$$4B' - C' - A' = 2\gamma^2 + \frac{10}{3} \delta^2 \quad (6.47)$$

$$4C' - A' - B' = 2\gamma^2 - \frac{10}{3} \delta^2 \quad (6.48)$$

Equation (6.42) can be rewritten upon substitution of these results as

$$\begin{aligned} |S_{if}|^2 &= \left(\frac{45a^2 - 2\gamma^2}{45} \right) |\hat{\xi} \cdot \hat{\xi}_s^*|^2 + \left(\frac{3\gamma^2 + 5\delta^2}{45} \right) |\hat{\xi}|^2 |\hat{\xi}_s|^2 \\ &\quad + \left(\frac{3\gamma^2 - 5\delta^2}{45} \right) |\hat{\xi} \cdot \hat{\xi}_s|^2 \end{aligned} \quad (6.49)$$

Upon substitution of Eq (6.49) into Eq (6.36), the Raman differential cross section becomes

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega} \right)_{fi} &= N_p \frac{\omega_s^4}{c^4} \left[\left(\frac{45a^2 - 2\gamma^2}{45} \right) |\hat{\xi} \cdot \hat{\xi}_s^*|^2 + \left(\frac{3\gamma^2 + 5\delta^2}{45} \right) |\hat{\xi}|^2 |\hat{\xi}_s|^2 \right. \\ &\quad \left. + \left(\frac{3\gamma^2 - 5\delta^2}{45} \right) |\hat{\xi} \cdot \hat{\xi}|^2 \right] \end{aligned} \quad (6.50)$$

This equation clearly shows the dependence of the Raman differential scattering cross section on the direction of observation and the polarization of the incident and scattered radiation. These parameters serve to define the vector description of $\hat{\xi}$ and $\hat{\xi}_s$ and therefore specific cross sections of interest.

Several differential cross sections are especially useful. Two cases which are frequently measured for linearly polarized radiation and often available from the literature are derived. For both of these cross sections, the direction of observations is perpendicular

to the direction of propagation of the incident beam and thus defines the scattering plane. In the first case, the incident radiation is polarized perpendicular to this scattering plane. The cross sections of interest are those measured with a polarizer perpendicular and parallel to the scattering plane. The notation used to distinguish these cases is $(\frac{d\sigma}{d\Omega})_{fi}(\xi, \hat{\xi}_s)$ where the dependence reflects the angle the field polarization makes with the scattering plane. For $(\frac{d\sigma}{d\Omega})_{fi}(\perp, \perp)$, $\hat{\xi}_s$ is parallel to $\hat{\xi}$ and from Eq (6.38)

$$(\frac{d\sigma}{d\Omega})_{fi}(\perp, \perp) = N \rho_{ii}^o \frac{\omega_s^4}{c^4} \frac{45a^2 + 4\gamma^2}{45} \quad (6.51)$$

For $(\frac{d\sigma}{d\Omega})_{fi}(\perp, \parallel)$, $\hat{\xi}_s$ is perpendicular to $\hat{\xi}$ with the result

$$(\frac{d\sigma}{d\Omega})_{fi}(\perp, \parallel) = N \rho_{ii}^o \frac{\omega_s^4}{c^4} \frac{3\gamma^2 + 5\delta^2}{45} \quad (6.52)$$

The depolarization ratio, $\rho_D(\hat{\xi})$, defined by

$$\rho_D(\hat{\xi}) = (\frac{d\sigma}{d\Omega})_{fi}(\hat{\xi}, \parallel) / (\frac{d\sigma}{d\Omega})_{fi}(\hat{\xi}, \perp) \quad (6.53)$$

becomes

$$\rho_D(\perp) = \frac{3\gamma^2 + 5\delta^2}{45a^2 + 4\gamma^2} \quad (6.54)$$

When the incident radiation is polarized parallel to the scattering plane

$$(\frac{d\sigma}{d\Omega})_{fi}(\parallel, \perp) = N \rho_{ii}^o \left(\frac{\omega_s}{c} \right)^4 \left(\frac{3\gamma^2 + 5\delta^2}{45} \right) \quad (6.55)$$

$$(\frac{d\sigma}{d\Omega})_{fi}(\parallel, \parallel) = N \rho_{ii}^o \left(\frac{\omega_s}{c} \right)^4 \left(\frac{3\gamma^2 + 5\delta^2}{45} \right) \quad (6.56)$$

$$\rho_D (||) = 1 \quad (6.57)$$

The Raman differential scattering cross section of Eq (6.50) can be written in terms of the two measured cross sections $(\frac{d\sigma}{d\Omega})_{fi} (\perp, \perp)$ and $(\frac{d\sigma}{d\Omega})_{fi} (\perp, ||)$ of Eqs (6.51) and (6.52) for linearly polarized light ($\xi_s = \xi_s^*$)

$$(\frac{d\sigma}{d\Omega})_{fi} = (\frac{d\sigma}{d\Omega})_{fi} (\perp, ||) + [(\frac{d\sigma}{d\Omega})_{fi} (\perp, \perp) - (\frac{d\sigma}{d\Omega})_{fi} (\perp, ||)] |\hat{\xi} \cdot \hat{\xi}_s|^2 \quad (6.58)$$

This shows that from measurements made of the differential scattering cross section using linearly polarized light, only two unique values may be obtained. It is, therefore, not possible to determine the three rotational invariants using only linearly polarized scattering. A similar result by Monson and McClain (Ref 93:32) for the two photon cross section led them to the use of circularly polarized light to measure a third independent value. The use of circularly polarized light for the Raman differential cross section also enables the measurement of a third independent value. Circularly polarized light is defined here as

$$\text{Left: } \hat{\xi} = \frac{1}{\sqrt{2}} (\hat{e}_1 + i \hat{e}_2) \quad \text{propagating along } \hat{e}_3 \quad (6.59)$$

$$\text{Right: } \hat{\xi} = \frac{1}{\sqrt{2}} (\hat{e}_1 - i \hat{e}_2) \quad \text{propagating along } \hat{e}_3 \quad (6.60)$$

A third measurement where both $\hat{\xi}$ and $\hat{\xi}_s$ have opposite circular polarization but propagate in the same direction is necessary. Any other combination of linear and circular polarizations provide a dependent value. To show this, assume that $\hat{\xi}$ is left circularly polarized along the z axis and $\hat{\xi}_s$ is right circularly polarized along the z axis.

$$\hat{\xi} = -\frac{1}{\sqrt{2}} (\hat{e}_x + i \hat{e}_y) \quad (6.61)$$

$$\hat{\xi}_s = -\frac{1}{\sqrt{2}} (\hat{e}_x - i \hat{e}_y) \quad (6.62)$$

then

$$\hat{\xi} \cdot \hat{\xi}_s^* = \frac{1}{2} (\hat{e}_x + i \hat{e}_y) \cdot (\hat{e}_x + i \hat{e}_y) = \frac{1}{2} (1 + i^2) = 0 \quad (6.63)$$

$$\hat{\xi} \cdot \hat{\xi}_s = \frac{1}{2} (\hat{e}_x + i \hat{e}_y) \cdot (\hat{e}_x - i \hat{e}_y) = \frac{1}{2} (1 - i^2) = 1 \quad (6.64)$$

Substituting these results into Eq (6.50) to obtain $(\frac{d\sigma}{d\Omega})_{fi} (L,R)$

$$(\frac{d\sigma}{d\Omega})_{fi} (L,R) = N\rho_{ii}^0 \left(\frac{\omega_s}{c} \right)^4 \left[\frac{3\gamma^2 + 5\delta^2}{45} + \frac{3\gamma^2 - 5\delta^2}{45} \right] \quad (6.65)$$

$$(\frac{d\sigma}{d\Omega})_{fi} (L,R) = N\rho_{ii}^0 \left(\frac{\omega_s}{c} \right)^4 \frac{6\gamma^2}{45} \quad (6.66)$$

or

$$\frac{6\gamma^2}{45} = \left(\frac{c}{\omega_s} \right)^4 \frac{1}{N\rho_{ii}^0} (\frac{d\sigma}{d\Omega})_{fi} (L,R) = (\frac{d\sigma}{d\Omega})_{fi} (L,R) \quad (6.67)$$

and from Eqs (6.51) and (6.52)

$$\frac{3\gamma^2 + 5\delta^2}{45} = (\frac{d\sigma}{d\Omega})_{fi} (\perp, \parallel) \quad (6.68)$$

$$\frac{45a^2 + 4\gamma^2}{45} = (\frac{d\sigma}{d\Omega})_{fi} (\perp, \perp) \quad (6.69)$$

The solution of these three equations for a^2 , γ^2 and δ^2 gives

$$a^2 = \left(\frac{c}{\omega_s} \right)^4 \frac{1}{N\rho_{fi}^0} \left[(\frac{d\sigma}{d\Omega})_{fi} (\perp, \perp) - \frac{2}{3} (\frac{d\sigma}{d\Omega})_{fi} (L,R) \right] \quad (6.70)$$

$$\gamma^2 = \left(\frac{c}{\omega_s}\right)^4 \frac{1}{N\rho_{ii}^0} \left[\frac{15}{2} \left(\frac{d\sigma}{d\Omega} \right)_{fi} (L,R) \right] \quad (6.71)$$

$$\delta^2 = \left(\frac{c}{\omega_s}\right)^4 \frac{1}{N\rho_{ii}^0} \left[9 \left(\frac{d\sigma}{d\Omega} \right)_{fi} (\perp, \parallel) - \frac{1}{2} \left(\frac{d\sigma}{d\Omega} \right)_{fi} (L,R) \right] \quad (6.72)$$

Thus the rotational invariants can be uniquely determined.

The analysis of Monson and McClain (Ref 93:33) on the symmetry properties of transitions from a totally symmetric ground state for their matrix elements is extended here to the polarizability matrix elements. The differential scattering cross section, $(\frac{d\sigma}{d\Omega})$ is proportional to $\overline{|S_{if}|^2}$ which can be rewritten from Eq (6.42) as

$$\begin{aligned} \overline{|S_{if}|^2} &= \frac{1}{30} \left[p_{\alpha\alpha} p_{\beta\beta}^* (4 |\hat{\xi} \cdot \hat{\xi}_s^*| - 1 - |\hat{\xi} \cdot \hat{\xi}_s|^2) \right. \\ &\quad + p_{\alpha\beta} p_{\alpha\beta}^* (- |\hat{\xi} \cdot \hat{\xi}_s^*| + 4 - |\hat{\xi} \cdot \hat{\xi}_s|^2) \\ &\quad \left. + p_{\alpha\beta} p_{\beta\alpha}^* (- |\hat{\xi} \cdot \hat{\xi}_s^*| - 1 + 4 |\hat{\xi} \cdot \hat{\xi}_s|^2) \right] \end{aligned} \quad (6.73)$$

where $|\xi|^2 = |\xi_s|^2 = 1$ has been used and the frequency dependence is suppressed. In this form, the ORS polarizability factors ($p_{\alpha\alpha} p_{\beta\beta}^*$, $p_{\alpha\beta} p_{\alpha\beta}^*$ and $p_{\alpha\beta} p_{\beta\alpha}^*$) are similar to the two photon absorption factors of Monson and McClain. When their analysis of the two photon factors is applied to the polarizability factors expressed in terms of the polarizability invariants, several useful results are obtained.

(1) $p_{\alpha\alpha} p_{\beta\beta}^*$: If the excited state transforms like xy , yz , or

z_x , a^2 vanishes. The same result of Placzek that restricts a^2 to the Q branch.

- (2) $p_{\alpha\beta} p_{\alpha\beta}^* - p_{\alpha\beta} p_{\beta\alpha}^*$: If the transition preserves the symmetry, δ is zero. That is to say the polarizability tensor has only symmetric properties as previously noted.
- (3) $p_{\alpha\alpha} p_{\beta\beta}^*$ and $p_{\alpha\beta} p_{\beta\alpha}^*$: If near electronic state resonance scattering occurs

$$9a^2 = \gamma^2 - \delta^2 \quad (6.74)$$

Then measurements using only linearly polarized light are sufficient to determine a^2 , γ^2 and δ^2 .

These results which can be used to obtain experimental parameters to calculate the third order susceptibilities show the care that must be taken in identifying all three of the experimental parameters. Equation (6.50) is capable of handling every possible polarization (linear or circular) and every possible direction of observation. It is only necessary to carefully define the incident and scattered radiation polarizations. From this single equation, it is possible to produce the four tables of Long (Ref 83:CRS 6).

The dependence of the rotational invariants on the set of quantum numbers specifying the energy state of the molecule and the requirement to specify the line or branch used was discussed above. It is possible, however, to provide scaling rules for the polarizability invariant parameters referenced to the $v = 0, J = 0$ set of parameters. The v scaling is that presented in Chapter V and summarized in

Table VI. The J dependence was derived for a symmetric polarizability (α^2 and γ^2) by Placzek (Ref 76). These results for the case where component of the total electronic angular momentum along the internuclear axis is quantized by the number K are

$$\gamma^2(J, K) = b_{J-K}^{JK} \gamma^2(0, 1) \quad (6.75)$$

$$\alpha^2(J, K) = \alpha^2 \delta_{JK}^{JK'} \quad \Delta M = 0 \quad (6.76)$$

The expressions for b_{J-K-J}^{JK} , taken from Placzek (Ref 76) are presented in Table VII. The case for $K=0$, b_J^J , is obtained from Table VII using the values for $K \rightarrow K' = K$ and setting $K=0$. This case assumes that in addition to zero electronic angular momentum about the internuclear axis, there is zero net electron spin. For the transitions $J \rightarrow J-1$ and $J \rightarrow J-2$, the b values may be derived from

$$(2J + 1) b_{J-K}^{JK} = (2J'+1) b_{JK}^{JK'} \quad (6.77)$$

Equation (6.76) states the result that isotropic (or trace) scattering can only occur when there is no change in the angular momentum quantum numbers, i.e., ($\Delta J=0$, $\Delta M=0$, $\Delta N=0$). Therefore, isotropic scattering lines only exist in the Q branch.

While Placzek derived the above scaling relations for a symmetric polarizability tensor, no similar results were found for the antisymmetric rotational invariant, δ^2 . However, because of the similarity of the form of δ^2 to γ^2 (compare Eqs (4.82) and (4.83)), the scaling on δ^2 is taken to be the same as that for γ^2 . δ^2 is not required in most instances of CARS scattering without electronic resonance enhancement.

TABLE VII Scaling Factor $b_{J', K'}^{J, K}$ ($J + J' \geq 2$)

| J' | J | $J+1$ | $J+2$ |
|-------|---|--|---|
| K' | | | |
| $K=0$ | $\frac{J(J+1)}{J(J+1)(2J-1)(2J+3)} - \frac{3K^2J^2}{J(J+1)(2J-1)(2J+3)}$ | $\frac{3K^2[(J+1)^2 - K^2]}{J(J+1)(J+2)(2J+1)}$ | $\frac{3[(J+1)^2 - K^2][(J+2)^2 - K^2]}{2(J+1)(J+2)(2J+1)(2J+3)}$ |
| $K+1$ | $\frac{3(2K+1)^2(J-K)}{2J(J+1)(2J-1)(2J+3)} \frac{(J+K+1)}{(J+1)(J+2)(2J+1)}$ | $\frac{(J+2K)^2(J+K+1)}{2J(J+1)(J+2)(2J+1)} \frac{(J+K+2)}{(J+1)(J+2)(2J+1)}$ | $\frac{[(J+1)^2 - K^2](J+K+2)(J+K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$ |
| $K-1$ | $\frac{3(2K-1)^2(J+K)}{2J(J+1)(2J-1)(2J+3)} \frac{(J-K+1)}{(J+1)(J+2)(2J+1)}$ | $\frac{(J+2K)^2(J-K+1)}{2J(J+1)(J+2)(2J+1)} \frac{(J-K+2)}{(J+1)(J+2)(2J+1)}$ | $\frac{[(J+1)^2 - K^2](J-K+2)(J-K+3)}{(J+1)(J+2)(2J+1)(2J+3)}$ |
| $K+2$ | $\frac{3[J^2 - (K+1)^2][J+1]^2 - (K+1)^2}{2J(J+1)(2J-1)(2J+3)}$ | $\frac{[(J+1)^2 - (K+1)^2](J+K+1)}{2J(J+1)(J+2)(2J+1)} \frac{(J+K+3)}{(J+1)(J+2)(2J+1)}$ | $\frac{(J+K+1)(J+K+2)(J+K+3)(J-K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$ |
| $K-2$ | $\frac{3[J^2 - (K-1)^2][J+1]^2 - (K-1)^2}{2J(J+1)(2J-1)(2J+3)}$ | $\frac{[(J+1)^2 - (K-1)^2](J-K+1)}{2J(J+1)(J+2)(2J+1)} \frac{(J-K+3)}{(J+1)(J+2)(2J+1)}$ | $\frac{(J-K+1)(J-K+2)(J-K+3)(J-K+4)}{4(J+1)(J+2)(2J+1)(2J+3)}$ |

From (Ref 76:225)

Furthermore, since $a^2: \gamma^2: \delta^2 = 1:10^{-2}:10^{-4}$, the scaling should not be a critical correction in using CARS as a diagnostic tool.

One other form of energy state dependence is necessary if calculations of cross sections are to be performed. This is the dependence of the population of molecular states, ρ_{ii}^0 . These are available from many references and are cited here for completeness. In general, for the ground electronic state

$$\rho_{ii}^0 = \varsigma e^{-E_i/kT} \quad (6.78)$$

where

$$E_i = E_{vib} + E_{rot} (J,K) \quad (6.79)$$

$E_{rot} (J,K) = E_{JK}$ = rotational energy of the molecule

$$\varsigma = g_I G_{JK} / \sum_{v,J} g_I G_{JK} e^{-(E_v + E_{JK})/kT} \quad (6.80)$$

g_I = statistical weight due to nuclear spin

G_{JK} = statistical weight due to the degeneracy of the rotational level.

The values for E_v , E_{JK} , g_I , and G_{JK} depend upon the class of the molecule (diatomic, linear, symmetric top, etc.). For completeness, the method of obtaining these quantities for the diatomic molecule is presented here. For the more complex molecules, reference should be made to Herzberg (Ref 94). The vibrational energy, E_v , is given by Eq (5.52)

$$E_v/hc = G(v) = v_e(v+1/2) - v_e x_e(v+1/2)^2 + v_e y_e(v+1/2)^3 + \dots \quad (5.52)$$

and the rotational energy in a similar manner by

$$E_J/hc = F_v(J) = B_v J(J+1) - D_v J^2(J+1)^2 \quad (6.81)$$

where

$$B_v = B_e - \alpha_e(v+1/2) \quad (6.82)$$

$$D_v = D_e + \beta_e(v+1/2) \quad (6.83)$$

The constants B_e , α_e , D_e and β_e are experimentally determined just as those are in Eq (5.52). The total energy, for the ground electronic state, is then determined by combining Eqs (5.52) and (6.81).

$$\begin{aligned} E_i/hc = T(v,J) = & v_e(v+1/2) - v_e x_e(v+1/2)^2 + v_e y_e(v+1/2)^3 \\ & + B_v J(J+1) - D_v J^2(J+1)^2 \end{aligned} \quad (6.84)$$

For a diatomic molecule (any linear molecule) the statical weight due to the rotational level degeneracy in energy is

$$g_J = 2J+1 \quad (6.85)$$

The nuclear spin statistical weight is not a single value for all nuclear combinations of even the diatomic molecules. g_I has the same value for all J levels of the heteronuclear diatomic molecules.

$$g_I = (2I_1+1)(2I_2+1) \quad (6.86)$$

However, for homonuclear diatomic molecules ($I_1 = I_2 = I$) g_I depends on the statistics of the nucleus (Bose-Einstein or Fermi-Dirac) and the symmetry of the J level for $\Lambda = 0$. To determine the symmetry, the coordinate wave function, ψ_c , is taken to be (a first order

approximation)

$$\psi_c = \psi_e \frac{1}{q} \psi_v \psi_j \quad (6.87)$$

where

ψ_e = electronic wavefunction

ψ_v = vibrational wavefunction

ψ_j = rotational wavefunction

The symmetry of ψ then depends on a reflection at the origin. Since $\frac{1}{q} \psi_v$ depends only on $|q|$, it is always unchanged by such a reflection and ψ_e and ψ_j determine the symmetry property of ψ_c . For ψ_e positive (symmetric), the symmetry of ψ depends directly on ψ_j only: ψ_j is positive when J even and negative when J odd. For ψ_e negative (antisymmetric), the symmetry of ψ_c depends on ψ_j as; symmetric for J odd and antisymmetric for J even. When a nuclear wavefunction ψ_N is defined, the total wavefunction, ψ , is

$$\psi = \psi_c \psi_N \quad (6.88)$$

and the total nuclear spin is given by T . Based upon experiment, it is known that nuclei with half-integer spins obey Fermi-Dirac statistics and those with whole integer spins obey Bose-Einstein statistics. Table VIII taken from published data (Ref 91:138) provides a ready reference to obtain $g_I(J)$ once the nuclear spin and the electronic wavefunction parity is known. The nuclear spin values for many nuclei are given by Melissinos (Ref 95:502).

TABLE VIII. Nuclear Spin Statistical Weight, g_I , for Homonuclear Molecules

| SPIN I: STATISTICS APPLICABLE | TOTAL PARITY (ψ) | ELECTRONIC WAVE FUNCTION PARITY (ψ_e) | J VALUE | COORDINATE WAVE FUNCTION PARITY (ψ_c) | NUCLEAR SPIN PARITY (ψ_n) | STATISTICAL WEIGHT, g_I | TOTAL NUCLEAR SPIN, I |
|-------------------------------------|-------------------------------|--|------------|--|---|------------------------------|-------------------------------|
| | | Antisym (-) | Odd | Sym (+) | Antisym (-) | $(2I+1) I$ | $2I-1, 2I-3, \dots$ |
| | | | Even | Antisym (-) | Sym (+) | $(2I+1)(I+1)$ | $2I, 2I-2, \dots$ |
| HALF- INTEGER: FERMI | Antisym (-) | Sym (+) | Odd | Antisym (-) | Sym (+) | $(2I+1)(I+1)$ | $2I, 2I-2, \dots$ |
| | | | Even | Sym (+) | Antisym (-) | $(2I+1) I$ | $2I-1, 2I-3, \dots$ |
| | | | Odd | Sym (+) | Sym (+) | $(2I+1)(I+1)$ | $2I, 2I-2, \dots$ |
| | | Antisym (-) | | | Antisym (-) | $(2I+1) I$ | $2I-1, 2I-3, \dots$ |
| INTEGER: BOSE | Sym (+) | | Even | Antisym (-) | Antisym (-) | $(2I+1) I$ | $2I-1, 2I-3, \dots$ |
| | | Sym (+) | Odd | Antisym (-) | Antisym (-) | $(2I+1) I$ | $2I-1, 2I-3, \dots$ |
| | | | Even | Sym (+) | Sym (+) | $(2I+1)(I+1)$ | $2I, 2I-2, \dots$ |

From (91:138)

VII. Macroscopic Equations

Medium Polarization

The orientational averaging results can now be applied to the dipole moments/molecular polarizabilities of Chapter IV. This provides the medium nonlinear polarization for each of the processes being considered. These nonlinear medium polarizations are valid for any field polarization (linear, circular or elliptical) and can therefore be used to describe any of the variations of CARS depending on field polarization (e.g., BOXCARS). To take advantage of the experimental information contained in the macroscopic Raman polarizability elements (or differential scattering cross section), the third order polarizabilities are expressed in terms of these Raman polarizability elements (Appendix G). For the third order polarizabilities to be in this form, the f and g factors must be equal (Appendix F). For the multifrequency case, the assumption of importance is: The frequency differences within the field bandwidth are either sufficiently less than the transition frequency to be ignored, or, the term is off resonance and becomes part of the nonresonant contribution. The results obtained apply, to a good first approximation, for electronic resonance enhancement when used with care. To keep the notation simple, a single resonant term from the sum for the multiresonant situation is used. The remainder of terms can be described by proper adjustment of the notation and incorporation of the summation. The most general form of the equations is derived before any simplifying assumptions are made. This provides a set of equations for the nonlinear polarization having the widest range of application. The development

of two of the nonlinear polarization vectors are treated in detail. These two, $p^{\text{SRS-S}(2)}$ and $p^{\text{CARS}(3)}$, are the polarizations most often used and serve to illustrate and describe the derivation of all sixteen polarization vectors obtained. The results for the sixteen polarization vectors are presented in Appendix J. A discussion of the additional equations needed to solve for the spectral intensity is included.

The derivation of the third order polarization starts with Eq (6.19). The expression for the polarizability is found from the tables in Appendix G and the vector coefficients A, B, and C from Eqs (6.20), (6.21) and (6.22). The single third order molecular polarizability term for the SRS-S process centered at a frequency ω_2 from Appendix G, Table G VI is

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}(2)} = K \ p_{\mu\alpha_2}^{\omega'''} p_{\alpha_3\alpha_1}^{*\omega'} \quad (7.1)$$

where

$$K_1 = \frac{\Delta_t}{6\hbar D_1} \quad (7.2)$$

$$D_1 = \omega_t + \omega' + \omega''' + i\Gamma_t \quad (7.3)$$

$$\Delta_t = \rho_v^0 - \rho_v^0 \quad (7.4)$$

The overall frequency dependence of $p^{\text{SRS-S}}$ is suppressed for notational convenience and the subscript t is used to represent the complete set. When the full frequency dependence is omitted, the central frequency is represented by a positive quantity. The vector

coefficient terms are obtained from Eq (7.1) as

$$p_{\mu\mu\alpha\alpha}^{\text{SRS-S}(2)} = K_1 p_{\mu\alpha}^{\omega''} p_{\alpha\mu}^{*-*\omega'} \quad (7.5)$$

$$p_{\mu\alpha\mu\alpha}^{\text{SRS-S}(2)} = K_1 p_{\mu\mu}^{\omega''} p_{\alpha\alpha}^{*-*\omega'} \quad (7.6)$$

$$p_{\mu\alpha\alpha\mu}^{\text{SRS-S}(2)} = K_1 p_{\mu\alpha}^{\omega''} p_{\mu\alpha}^{*-*\omega'} \quad (7.7)$$

The vector coefficients are

$$A(\omega_2) = K_1 (4p_{\mu\alpha} p_{\alpha\mu}^* - p_{\mu\mu} p_{\alpha\alpha}^* - p_{\mu\alpha} p_{\mu\alpha}^*) \quad (7.8)$$

$$-B(\omega_2) = K_1 (4p_{\mu\mu} p_{\alpha\alpha}^* - p_{\mu\alpha} p_{\mu\alpha}^* - p_{\mu\alpha} p_{\alpha\mu}^*) \quad (7.9)$$

$$-C(\omega_2) = K_1 (4p_{\mu\alpha} p_{\mu\alpha}^* - p_{\mu\alpha} p_{\alpha\mu}^* - p_{\mu\mu} p_{\alpha\alpha}^*) \quad (7.10)$$

where the frequency superscripts are implied, $-\omega'$ is associated with the conjugate and ω'' the other p_{ij} term. A set of pseudo-polarizability invariants for this set of Raman polarizability tensor element products can be defined similar to those for ORS, Eqs (4.81), (4.82) and (4.83). For example

$$9 a_s^2 = (p_{11} + p_{22} + p_{33})(p_{11}^* + p_{22}^* + p_{33}^*) = p_{\mu\mu}^{\omega''} p_{\alpha\alpha}^{*-*\omega'} \quad (7.11)$$

Equations (6.43), (6.44) and (6.45) then provide the result

$$p_{\mu\mu} p_{\alpha\alpha}^* = 9a_s^2 \quad (7.12)$$

$$p_{\mu\alpha} p_{\mu\alpha}^* = 3a_s^2 + \frac{2}{3} \gamma_s^2 + \frac{2}{3} \delta_s^2 \quad (7.13)$$

$$p_{\mu\alpha} p_{\alpha\mu}^* = 3a_s^2 + \frac{2}{3} \gamma_s^2 - \frac{2}{3} \delta_s^2 \quad (7.14)$$

Upon substitution of these values into A, B and C and use of Eqs (6.27), (6.28), and (6.29), the susceptibilities are

$$x_{1122}^{\text{SRS-S}(2)} = NK_1 \frac{3\gamma_s^2 - 5\delta_s^2}{45} + x_{1122}^{\text{NR}} \quad (7.15)$$

$$x_{1212}^{\text{SRS-S}(2)} = NK_1 \frac{45a_s^2 - 2\gamma_s^2}{45} + x_{1212}^{\text{NR}} \quad (7.16)$$

$$x_{1221}^{\text{SRS-S}(2)} = NK_1 \frac{3\gamma_s^2 - 5\delta_s^2}{45} + x_{1221}^{\text{NR}} \quad (7.17)$$

The nonresonant terms, left in Eq (4.21) after removal of the resonant terms, cannot be written as products of the Raman polarizability tensor elements. These terms do have dipole matrix element sums that must be included in the averaged susceptibility. Because these remaining terms are usually far from resonance, the imaginary term is small and often ignored. The result of the averaging to obtain the susceptibilities for the nonresonant terms is represented by x^{NR} and it is assumed real. Since the resonant susceptibilities are different, it is expected that the nonresonant terms are also different. The isotropic conditions do hold for the nonresonant susceptibilities.

The polarization integrand, P^I , with the frequency dependence shown is then determined from Eq (6.19) for the fields and vector components of the SRS-S term of Eq (4.46).

$$\begin{aligned}
P^I(\omega_2) = & \left\{ \left[NK_1(\omega', \omega''') - \frac{3\gamma_s^2(\omega'', -\omega') - 5\delta_s^2(\omega'', -\omega')}{45} + x_{1122}^{NR} \right] (\hat{a}_1 \cdot \hat{a}_2) \hat{a}_1^* \right. \\
& + \left[NK_1(\omega', \omega''') - \frac{45a_s^2(\omega'', -\omega') - 2\gamma_s^2(\omega'', -\omega')}{45} + x_{1212}^{NR} \right] (\hat{a}_1^* \cdot \hat{a}_2) \hat{a}_1 \\
& \left. + \left[NK_1(\omega', \omega''') - \frac{3\gamma_s^2(\omega'', -\omega') + 5\delta_s^2(\omega'', -\omega')}{45} + x_{1221}^{NR} \right] (\hat{a}_1^* \cdot \hat{a}_1) \hat{a}_2 \right\} \\
& \times \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \delta(\omega - \omega' - \omega'' - \omega''')
\end{aligned} \tag{7.18}$$

and

$$\begin{aligned}
P^{SRS-S(2)} = & 6 \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' P^I(\omega_2) \\
P^{SRS-S(2)} = & 6 \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \\
& \left\{ \left[x_{1122}^{SRS-S(2)}(-\omega; \omega', \omega'', \omega''') + x_{1122}^{NR} \right] (\hat{a}_1 \cdot \hat{a}_2) \hat{a}_1^* \right. \\
& + \left[x_{1212}^{SRS-S(2)}(-\omega; \omega', \omega'', \omega''') + x_{1212}^{NR} \right] (\hat{a}_1^* \cdot \hat{a}_2) \hat{a}_1 \\
& \left. + \left[x_{1221}^{SRS-S(2)}(-\omega; \omega', \omega'', \omega''') + x_{1221}^{NR} \right] (\hat{a}_1^* \cdot \hat{a}_1) \hat{a}_2 \right\} \\
& \times \epsilon_1^*(-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') \delta(\omega - \omega' - \omega'' - \omega''')
\end{aligned} \tag{7.20}$$

where

$$x_{1122}^{\text{SRS-S(2)}}(-\omega; \omega', \omega'', \omega''') = \frac{N\Delta_t}{6h} \frac{3\gamma_s^2(\omega'', -\omega') - 5\delta_s^2(\omega'', -\omega')}{45(\omega_t + \omega' + \omega''' + i\Gamma_t)} \quad (7.21)$$

$$x_{1212}^{\text{SRS-S(2)}}(-\omega; \omega', \omega'', \omega''') = \frac{N\Delta_t}{6h} \frac{45a_s^2(\omega'', -\omega') - 2\gamma_s^2(\omega'', -\omega')}{45(\omega_t + \omega' + \omega''' + i\Gamma_t)} \quad (7.22)$$

$$x_{1221}^{\text{SRS-S(2)}}(-\omega; \omega', \omega'', \omega''') = \frac{N\Delta_t}{6h} \frac{3\gamma_s^2(\omega'', -\omega') + 5\delta_s^2(\omega'', -\omega')}{45(\omega_t + \omega' + \omega''' + i\Gamma_t)} \quad (7.23)$$

These results are entirely general in terms of frequency dependence, field distribution in frequency space, type and direction of field polarization, and type of molecular transition allowed. Some special cases that have general applicability are treated in the next section.

Proceeding in a similar manner, the nonlinear polarization can be obtained for $P^{\text{CARS(3)}}$. From Appendix G, Table G X

$$P_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS(3)}} = K_2 P_{\alpha_1\alpha_2}^{\omega''} P_{\alpha_3\mu}^{*\omega} + K_3 P_{\alpha_1\alpha_3}^{\omega'''} P_{\alpha_2\mu}^{*\omega} \quad (7.24)$$

where

$$K_2 = \frac{\Delta_t}{6hD_2} \quad (7.25)$$

$$D_2 = \omega_t - \omega' - \omega''' - i\Gamma_t \quad (7.26)$$

$$K_3 = \frac{\Delta_t}{6hD_3} \quad (7.27)$$

$$D_3 = \omega_t - \omega' - \omega''' - i\Gamma_t \quad (7.28)$$

The vector coefficient terms are

$$p_{\mu\mu\alpha\alpha}^{\text{CARS}(3)} = K_2 p_{\mu\alpha}^{\omega''} p_{\alpha\mu}^{*\omega} + K_3 p_{\mu\alpha}^{\omega'''} p_{\alpha\mu}^{*\omega} \quad (7.29)$$

$$p_{\mu\alpha\mu\alpha}^{\text{CARS}(3)} = K_2 p_{\alpha\mu}^{\omega''} p_{\alpha\mu}^{*\omega} + K_3 p_{\alpha\alpha}^{\omega'''} p_{\mu\mu}^{*\omega} \quad (7.30)$$

$$p_{\mu\alpha\alpha\mu}^{\text{CARS}(3)} = K_2 p_{\alpha\alpha}^{\omega''} p_{\mu\mu}^{*\omega} + K_3 p_{\alpha\mu}^{\omega'''} p_{\alpha\mu}^{*\omega} \quad (7.31)$$

Because of the similarity in the forms of the frequency dependence of the terms in these last equations and the integration over this frequency dependence, ω''' in the last term of each equation may be replaced with ω'' . After this change, the vector coefficients are

$$A(\omega_3) = 2K_2 (4p_{\mu\alpha}^* p_{\alpha\mu}^* - p_{\alpha\mu}^* p_{\alpha\mu}^* - p_{\alpha\alpha}^* p_{\mu\mu}^*) \quad (7.32)$$

$$-B(\omega_3) = K_2 (4p_{\alpha\mu}^* p_{\alpha\mu}^* - p_{\alpha\alpha}^* p_{\mu\mu}^* - p_{\mu\alpha}^* p_{\alpha\mu}^*) \quad (7.33)$$

$$+ K_2 (4p_{\alpha\alpha}^* p_{\mu\mu}^* - p_{\alpha\mu}^* p_{\alpha\mu}^* - p_{\mu\alpha}^* p_{\alpha\mu}^*)$$

$$-B(\omega_3) = K_2 (3p_{\alpha\mu}^* p_{\alpha\mu}^* + 3p_{\alpha\alpha}^* p_{\mu\mu}^* - 2p_{\mu\alpha}^* p_{\alpha\mu}^*) \quad (7.34)$$

$$-C(\omega_3) = K_2 (3p_{\alpha\mu}^* p_{\alpha\mu}^* + 3p_{\alpha\alpha}^* p_{\mu\mu}^* - 2p_{\mu\alpha}^* p_{\alpha\mu}^*) \quad (7.35)$$

The equality of $B(\omega_3)$ and $C(\omega_3)$ as shown supports the equality of the resonant susceptibilities

$$x_{1212}^{\text{CARS}(3)(-\omega; \omega', \omega'', \omega''')} = x_{1221}^{\text{CARS}(3)(-\omega; \omega', \omega'', \omega''')} \quad (7.36)$$

Defining a set of pseudo-polarizability invariants for this CARS expression as

$$p_{\alpha\alpha} p_{\mu\mu}^* = 9 a_c^2 \quad (7.37)$$

$$p_{\alpha\mu} p_{\alpha\mu}^* = 3 a_c^2 + \frac{2}{3} \gamma_c^2 + \frac{2}{3} \delta_c^2 \quad (7.38)$$

$$p_{\mu\alpha} p_{\alpha\mu}^* = 3 a_c^2 + \frac{2}{3} \gamma_c^2 - \frac{2}{3} \delta_c^2 \quad (7.39)$$

The susceptibility elements for this CARS(3) in terms of these invariants are

$$x_{1122}^{\text{CARS}(3)} = 2NK_2 \frac{3\gamma_c^2 - 5\delta_c^2}{45} + x_{1122}^{\text{NR}} \quad (7.40)$$

$$x_{1212}^{\text{CARS}(3)} = NK_2 \frac{45a_c^2 + \gamma_c^2 + 5\delta_c^2}{45} + x_{1212}^{\text{NR}} \quad (7.41)$$

$$x_{1221}^{\text{CARS}(3)} = NK_2 \frac{45a_c^2 + \gamma_c^2 + 5\delta_c^2}{45} + x_{1221}^{\text{NR}} \quad (7.42)$$

After using the order of the vector fields for the CARS term from Eq (4.47) in Eq (6.34)

$$\begin{aligned} \bar{p}^{\text{CARS}(3)} &= 3 \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \\ &\left\{ \begin{aligned} &\left[x_{1122}^{\text{CARS}(3)} (-\omega; \omega', \omega'', \omega''') + x_{1122}^{\text{NR}} \right] (\hat{a}_1 \cdot \hat{a}_1) \hat{a}_2^* \\ &+ \left[x_{1212}^{\text{CARS}(3)} (-\omega; \omega', \omega'', \omega''') + x_{1212}^{\text{NR}} \right] (\hat{a}_2^* \cdot \hat{a}_1) \hat{a}_1 \\ &+ \left[x_{1221}^{\text{CARS}(3)} (-\omega; \omega', \omega'', \omega''') + x_{1221}^{\text{NR}} \right] (\hat{a}_2^* \cdot \hat{a}_1) \hat{a}_1 \end{aligned} \right\} \\ &\times \epsilon_2^* (-\omega') \epsilon_1 (\omega'') \epsilon_1 (\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \quad (7.43) \end{aligned}$$

The polarization vector products for the last two terms in Eq (7.43) are equal and the terms can be combined. Equation (7.36) can be used to write the polarization as

$$\begin{aligned} \bar{p}_{\text{CARS}(3)} &= 3 \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \\ &\left\{ \left[x_{1122}^{\text{CARS}(3)}(-\omega; \omega', \omega'', \omega''') + x_{1122}^{\text{NR}} \right] (\hat{a}_1 \cdot \hat{a}_1) \hat{a}_2^* \right. \\ &\quad \left. + \left[2x_{1212}^{\text{CARS}(3)}(-\omega; \omega', \omega'', \omega''') + x_{1212}^{\text{NR}} + x_{1221}^{\text{NR}} \right] (\hat{a}_2 \cdot \hat{a}_1) \hat{a}_1^* \right\} \\ &\times \epsilon_2^*(\omega') \epsilon_1(\omega'') \epsilon_1(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \end{aligned} \quad (7.44)$$

where

$$x_{1122}^{\text{CARS}(3)}(-\omega; \omega', \omega'', \omega''') = \frac{N\Delta_t}{3\hbar} \frac{3\gamma_c^2(\omega, \omega'', \omega''') - 5\delta_c^2(\omega', \omega'', \omega''')}{45(\omega_t - \omega' - \omega'' - i\Gamma_t)} \quad (7.45)$$

$$x_{1212}^{\text{CARS}(3)}(-\omega; \omega', \omega'', \omega''') = \frac{N\Delta_t}{6\hbar} \frac{45a_c^2(\omega', \omega'', \omega''') + \gamma_c^2(\omega', \omega'', \omega''') + 5\delta_c^2(\omega', \omega'', \omega''')}{45(\omega_t - \omega' - \omega'' - i\Gamma_t)} \quad (7.46)$$

$$x_{1221}^{\text{CARS}(3)}(-\omega; \omega', \omega'', \omega''') = x_{1212}^{\text{CARS}(3)}(-\omega; \omega', \omega'', \omega''') \quad (7.47)$$

In these equations, the shorthand notation $\omega = \omega' + \omega'' + \omega'''$ on the polarizability tensor elements has been removed.

Appendix J contains the third order polarizations obtained using this approach for the six processes at the four frequencies. For each of the sixteen polarizations, the three resonant susceptibilities,

x_{1122} , x_{1212} and x_{1221} , are defined and the vector direction of each shown. Because the resonant susceptibilities can be written as functions of Raman polarizability tensor elements upon orientational averaging, the susceptibilities are expressable as functions of pseudo polarizability invariants, a_i^2 , γ_i^2 and δ_i^2 . Also, due to the averaging, these three invariants combine into three distinct sums:

$$\frac{3\gamma_i^2 - 5\delta_i^2}{45} ; \quad \frac{3\gamma_i^2 + 5\delta_i^2}{45} ; \quad \frac{45a_i^2 - 2\gamma_i^2}{45}$$

These are exactly the forms appearing in the ordinary Raman differential scattering cross section, Eq (6.50). Furthermore, the x_{1111}^i susceptibility element for every process takes the form

$$x_{1111}^i = K \frac{45a_i^2 + 4\gamma_i^2}{45} \quad (7.48)$$

This susceptibility element evolves for every process where the input field polarization vectors are parallel and is clearly the largest value a susceptibility element can have. Therefore, to maximize the output of an experiment, parallel inputs need to be used.

The rotational invariants for each of the processes are taken to scale the same as those for the Raman scattering case. The vibrational scaling is taken from Table VI and the rotational scaling from Eqs (6.75), (6.76) and (6.77). The antisymmetric invariant, δ^2 , is again assumed to scale like the isotropic one. The results are

$$a_i^2 = b_v^2 \quad a_i^2(v) \delta \frac{JKM}{J'K'M'} \quad (7.49)$$

$$\gamma_i^2 = b_v^2 b_{J-K}^{JK} \gamma_i^2 (v, J, K) \quad (7.50)$$

$$\delta_i^2 = b_v^2 b_{J-K}^{JK} \delta_i^2 (v, J, K) \quad (7.51)$$

b_{J-K}^{JK} is from Table VII.

The polarizability tensor elements in the dipole approximation are real, Eq (E31). This reality has been used to obtain the results tabulated in Appendix J. These results are in the form of the Raman polarizability invariants from Eqs (4.81), (4.82) and (4.83). When the reality condition is not applicable (e.g., in electronic resonance enhancement) greater care must be used to track the complex configuration on the polarizability elements. This is summarized in the following equations.

$$a(\omega_j) = \frac{1}{3} p_{\alpha\alpha}(\omega_j) \quad (7.52)$$

$$a^2(\omega_j) = \frac{1}{9} p_{\alpha\alpha}(\omega_j) p_{\beta\beta}^*(\omega_j) \quad (7.53)$$

$$a_i^2(\omega_j, \omega_k) = \frac{1}{9} p_{\alpha\alpha}(\omega_j) p_{\beta\beta}^*(\omega_k) \quad (7.54)$$

$$\gamma_i^2(\omega_j) = \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\alpha\beta}^*(\omega_j) + \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\beta\alpha}^*(\omega_j) - 2 p_{\alpha\alpha}(\omega_j) p_{\beta\beta}^*(\omega_j) \quad (7.55)$$

$$\gamma_i^2(\omega_j, \omega_k) = \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\alpha\beta}^*(\omega_k) + \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\beta\alpha}^*(\omega_k) - 2 p_{\alpha\alpha}(\omega_j) p_{\beta\beta}^*(\omega_k) \quad (7.56)$$

$$\delta^2(\omega_j) = \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\alpha\beta}^*(\omega_j) - \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\beta\alpha}^*(\omega_j) \quad (7.57)$$

$$\delta^2(\omega_j, \omega_k) = \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\alpha\beta}^*(\omega_k) - \frac{3}{4} p_{\alpha\beta}(\omega_j) p_{\beta\alpha}^*(\omega_k) \quad (7.58)$$

$$a_i^2(\omega_k, \omega_j) = [a_i^2(\omega_j, \omega_k)]^* \quad (7.59)$$

$$\gamma_{ij}^2(\omega_k, \omega_j) = [\gamma_{ij}^2(\omega_j, \omega_k)]^* \quad (7.60)$$

$$\delta_{ij}^2(\omega_k, \omega_j) = [\delta_{ij}^2(\omega_j, \omega_k)]^* \quad (7.61)$$

To place this effect in perspective, the isotropic invariant as a function of the central frequency, is shown in Table IX for each of the nonlinear processes. The conjugation is arbitrary, but should be done consistently.

| | SRS-S | CARS | SRS-P | CSRS | CMRS | SRS-SS |
|------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| ω_1 | $a^2(\omega_1, \omega_1)$ | $a^2(\omega_3, \omega_1)$ | $a^2(\omega_3, \omega_3)$ | $a^2(\omega_2, \omega_1)$ | $a^2(\omega_3, \omega_2)$ | |
| ω_2 | $a^2(\omega_1, \omega_1)$ | $a^2(\omega_1, \omega_3)$ | | $a^2(\omega_1, \omega_2)$ | $a^2(\omega_3, \omega_2)$ | $a^2(\omega_2, \omega_2)$ |
| ω_3 | | $a^2(\omega_1, \omega_3)$ | $a^2(\omega_3, \omega_3)$ | | $a^2(\omega_2, \omega_3)$ | |
| ω_4 | | | | $a^2(\omega_2, \omega_1)$ | $a^2(\omega_2, \omega_3)$ | $a^2(\omega_2, \omega_2)$ |

The equations obtained in this section provide a complete set of equations to determine the medium polarization for the six processes of Table V at the four frequencies $\omega_1, \omega_2, \omega_3$ and ω_4 . These equations are applicable over the broadest range of experimental conditions; arbitrary field vector polarizations, electronic resonance enhancement, multifrequency fields, or combinations thereof. The parameters

in the equations are well defined and traceable through the assumptions explicitly made to their source. Given the electric field distribution in frequency space, its vector polarization and the molecule of interest, the remaining parameters needed are accessible. That is not to say that the damping term, Γ_t , the transition frequency, ω_t , and the pseudo-polarizability invariant, a_i^2 , γ_i^2 and δ_i^2 , are all immediately available in the experimental literature. They are, however, readily available to a good approximation under many conditions of interest. The equations presented here, further, allow a determination of the sensitivity to these approximations over many experimental condition. Several of the situations that are encountered in using CARS and that simplify the equations are presented in the next section.

Medium Polarization: Special Cases

Symmetric Polarizability Tensor. A set of experimental conditions for which the polarizability tensor is symmetric were given in Chapter IV. These conditions apply to many of the experimental situations in which CARS or the other nonlinear processes are used. When these conditions do apply, the antisymmetric invariant is identically zero ($\delta_i^2=0$). This reduces the number of invariants to two and certainly simplifies the determination of both the Raman scattering cross section and the susceptibilities.

For the nonparametric third order processes, the results in Appendix J show an additional relation for two of the susceptibilities elements $x_{1122}^{SRS-i(j)}$ and $x_{1221}^{SRS-i(j)}$ when $\delta=0$.

$$x_{1122}^{SRS-i(j)}(-\omega; \omega', \omega'', \omega''') = x_{1221}^{SRS-i(j)}(-\omega; \omega', \omega'', \omega''') \quad (7.62)$$

The Raman cross section requires only the linear polarization vector measurements to determine the general form, Eq (6.50). For $\delta_i^2 = 0$,

$$(\frac{d\sigma}{d\Omega})_{fi} (L, R) = 2 (\frac{d\sigma}{d\Omega})_{fi} (L, ||) \quad (7.63)$$

In the next section, it is shown that zero antisymmetry simplifies the calculation of the medium polarization. In principle, it should be possible to use measurements from the nonparametric processes to determine the symmetry of a state. The limitation in practice would be in the accuracy provided by the experimental apparatus. Two exceptions to zero antisymmetry are a degenerate electronic ground state where the wavefunction is also degenerate (Ref 94:104) and a resonance of one of the fields with an electronic state.

Electronic Resonance. In the absence of electronic resonance enhancement of the third order processes, the polarizability tensor elements exhibit a very weak dependence on frequency. This is confirmed experimentally by the scaling of the Raman cross section with the fourth power of the scattered beam frequency. This is exactly the scaling predicted by Eq (6.50) when no frequency dependence of the polarizability tensor is considered. The polarizability tensor elements are approximately constant in this situation and so are the polarizability invariants, a_i^2 , γ_i^2 and δ_i^2 . The linear combination of these invariants in the third order susceptibilities (see tables in Appendix J) can then be set equal to the ordinary Raman polarizability invariants of Eqs (4.81), (4.82) and (4.83) and taken outside of the integral over frequency in Eq (J1). These Raman invariants are

related to a specific set of cross sections by Eqs (6.70), (6.71) and (6.72). The polarizability elements for use in the determination of the susceptibilities are then completely determined by experimentally available values.

Furthermore, when the polarizability tensor is symmetric, as in the previous section, the determination of part of the susceptibility is further simplified. For $\delta_i = 0$ and no electronic resonance enhancement

$$\gamma_i^2 = \gamma^2 = 15 \left(\frac{d\sigma}{d\Omega} \right)' (\perp, \parallel) \quad (7.64)$$

$$a_i^2 = a^2 = \left(\frac{d\sigma}{d\Omega} \right)' (\perp, \perp) - \frac{4}{3} \left(\frac{d\sigma}{d\Omega} \right)' (\perp, \parallel) \quad (7.65)$$

Or, if Eq (6.53) for the depolarization ratio is used

$$\gamma_i^2 = \gamma^2 = 15 \rho_D(\perp) \left(\frac{d\sigma}{d\Omega} \right)' (\perp, \perp) \quad (7.66)$$

$$a_i^2 = a^2 = \left(\frac{d\sigma}{d\Omega} \right)' (\perp, \perp) [1 - \frac{4}{3} \rho_D(\perp)] \quad (7.67)$$

where $\left(\frac{d\sigma}{d\Omega} \right)'$ is the cross section normalized with respect to frequency and number density. A typical ratio of a^2 to γ^2 is

$$a^2 : \gamma^2 \sim 10^2 : 1 \quad (7.68)$$

A significant amount of data is available for the depolarization ratio and the $\left(\frac{d\sigma}{d\Omega} \right) (\perp, \perp)$ cross section (Ref 96).

As a resonance with an electronic state is approached by an incident beam, the polarizability tensor element, p_{ij} , shows a significant frequency variation (Ref 90:204). In this situation, the

polarizability invariants can no longer be assumed independent of the frequency. The polarizability elements are still a good approximation if the difference of the frequencies in the f and g factors of Eq (4.74) is near both the Raman active resonance and the electronic resonance simultaneously. If one of the frequencies is in resonance with an electronic state but the frequency difference cannot be adequately approximated as that between the Raman active states, f does not equal g; the separate forms must then be retained. In this latter situation, the direct difference in the state population does not result but, rather the population density of each state must be treated separately. Additionally, the dipole matrix element sums that were lumped into the nonresonant susceptibility may also have terms with resonant denominators and their contribution to the process must be considered. These two effects significantly complicate any calculations. In general, when electronic resonance exists, the polarizability approximation fails. Druet and Taran have treated the electronic resonance enhancement for the monochromatic CARS process at ω_3 from a molecular point of view (Ref 97). In Raman scattering, similar resonance enhancement can occur and has been treated extensively in the literature (Ref 90 has an extensive bibliography). In the Raman case, the scattering cross section depends on the polarizability tensor elements to the second power through the polarizability invariants. This cross section therefore depends quadratically on the resonance term. In the parametric process, however, only one of the polarizability elements in the pseudo polarizability invariants contains the resonance and thus the susceptibility for these processes is linear in its

resonance dependence. It has been analytically shown under simplifying conditions that the beam intensity generated at the anti-Stokes frequency, ω_3 , depends on the square of the susceptibility and hence quadratically on the polarizability tensor element with the resonant denominator. An examination is needed for the electronic resonant terms in both x^i and x^{NR} to determine if resonance Raman cross sections can be used to evaluate the electronic resonance enhanced susceptibility similar to the off-resonance case. This could greatly simplify the calculation and provide a new source of experimental information for electronic enhanced CARS.

Field Vector Polarization. The results obtained in this research for the medium polarization are completely general in the selection of the field vector polarizations. This general applicability makes these equations useful in analyzing all vector polarization schemes for the six processes described. These vector polarization techniques range from the simplest condition of parallel linear polarization to the more complex ones such as multipolarized BOXCARS (Ref 98) and coherent Raman ellipsometry (Ref 99). The effect of the direction and form (linear versus circular) on the magnitude of the medium polarization and hence the beam intensity is also available from the set of equations derived. This is demonstrated by considering the field vector polarization to be both linear and parallel to each other. Because of its experimental simplicity, this is often the arrangement used in CARS measurements. The form of the susceptibility for each process becomes

$$\frac{n\Delta_t}{\hbar D} \quad \frac{1}{45} [45a_i^2 + 4Y_i^2] \quad (7.69)$$

which is exactly that of x_{1111}^i of Eq (7.48) and is thus the maximum possible value. Although this creates the maximum resonant susceptibility, it also produces the maximum nonresonant (or background) susceptibility. This is a limitation to the determination of molecular density in gas analysis.

Several polarization schemes have been proposed to reduce the background susceptibility (Ref 63, 98-101). The approach analyzed by Oudar (Ref 100; Ref 101 is the same technique) where only the CARS process is considered relies on the linear polarization vector differences to determine a null angle for the background susceptibility. The failure, experimentally, to observe complete cancellation of the background susceptibility effect was attributed to failure of Kleinman symmetry (Ref 102:1978) of the nonresonant susceptibility. But the results obtained here, Table JIII, show that there are contributions to the medium polarization at ω_3 due to the SRS-P and CMRS processes. Although these processes produce weaker effects than CARS in most experiments due to the relative field intensity dependence of the process, they may be of a magnitude off resonance comparable to or greater than the nonresonant susceptibility. These two extra processes certainly contain nonresonant susceptibilities themselves which must be accounted for in any cancellation analysis. A straight forward, although numerical, calculation of the effects of these additional processes would be worthwhile. The linear polarization approach of Eckbreth, BOXCARS, where different propagation vectors are used for the pump beams to provide spatial resolution (Ref 103) is more complex. The analysis of these cases follows naturally from the form of the equations derived. It is also possible to include not

only the effect of field vector polarization for each process but to also analyze the effects of nearby resonances as required in the ellipsometry approach of Akhmanov (Ref 99:672) using the equations herein. The form of these equations are also very useful in analyzing depolarization ratio measurements as suggested by Yuratich (Ref 104:679).

Field Frequency Distribution. The equations obtained in this research for the medium polarization apply to any nonoverlapping distribution of the field amplitude in frequency space. This was one of the goals of the work so that the multifrequency CARS approach could be analyzed. The monochromatic or near monochromatic case is easily obtained from this set of equations by the following equalities

$$\bar{\epsilon}_i(\omega') = \bar{A}_i \delta(\omega' - \omega_i) \quad (7.70)$$

$$\bar{\epsilon}_i^*(-\omega') = \bar{A}_i^* (\omega' + \omega_i) \quad (7.71)$$

When these delta functions are used, the form of the medium polarization required to describe most CARS experiments is obtained and the differences between multifrequency and monochromatic cases are clearly delineated. For the monochromatic, nonparametric (Stimulated Raman Scattering) processes, the polarizability invariants are precisely those for Raman scattering with the incident beam frequency corresponding to that of the annihilated photon. In such a case, an exact substitution of the normalized Raman differential scattering cross section is possible. The parametric processes when the fields are monochromatic do have a mixed frequency dependence for the polari-

zability invariants but there is only one set associated with each process (e.g., $a_i^2(\omega_1, \omega_3)$ for CARS). The susceptibility element x_{1111}^i for the parametric processes where frequency degeneracy exists (e.g., CARS and CSRS) is approximately twice that of nonparametric process. Since the multiplicative coefficient, K, in equation (J1), is three and six, respectively, this is a compensating effect. The field independent part of the medium polarization is approximately equal for all processes with collinear field polarization.

The CARS process at ω_1 , Table JI, and the CSRS process at ω_2 , Table JII, both have two resonant denominator forms in general field equations. Because of the occurrence of slightly different frequency differences in the multifrequency case, these two denominators will not have the same frequency dependence and a resultant "mixing" of each susceptibility occurs. When the fields are monochromatic, the frequency dependence of the two denominators is identical although they are complex conjugates of each other. The susceptibility tensor element x_{1122}^i is then real and x_{1212}^i and x_{1221}^i are complex conjugates of each other so that x_{1111}^i is real.

General Equations

Wave Equation. The research of this dissertation has concentrated on deriving nonlinear medium polarizations for use in interpreting laboratory experiments. To use these polarization equations in Appendix J, the wave equation and appropriate boundary conditions are necessary. A brief review of these is presented here along with some comments on the solution to obtain generated beam intensities. Two equations are required to predict accurately the

macroscopic behavior of the propagating fields and the media; the wave equation and the rate equation for the state population of the molecules. The wave equation is obtained in the standard manner from Maxwell's equations by eliminating \bar{B} from Eq (2.15a) using Eq (2.15b) with the result

$$\nabla \times \nabla \times \bar{E} + \frac{1}{c^2} \frac{\partial^2 \bar{E}}{\partial t^2} = -\frac{4\pi}{c^2} \frac{\partial \bar{P}}{\partial t^2} \quad (7.72)$$

Equation (2.15e) may be used to show explicitly the dependence on the nonlinear polarization

$$\nabla \times \nabla \times \bar{E} + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} (\bar{\epsilon} \cdot \bar{E}) = -\frac{4\pi}{c^2} \frac{\partial^2 \bar{P}^{NL}}{\partial t^2} \quad (7.73)$$

where Eq (2.9) has been used with

$$\bar{P}^L = \bar{\chi}^L \cdot \bar{E} \quad (7.74)$$

A wave equation can be written for each of the frequency components.

Equation (7.73) then becomes

$$\nabla \times [\nabla \times \bar{E}(\bar{r}, \omega_i, t)] + \frac{1}{c^2} \frac{\partial^2}{\partial t^2} [\bar{\epsilon} \cdot \bar{E}(\bar{r}, \omega_i, t)] = -\frac{4\pi}{c^2} \frac{\partial^2 \bar{P}^{NL}}{\partial t^2}(\bar{r}, \omega_i, t) \quad (7.75)$$

where the spatial and temporal dependence is explicitly shown. This can be Fourier transformed using Eq (3.1) to give the wave equation

$$\nabla \times [\nabla \times \bar{E}(\bar{r}, \omega_i)] - \frac{\omega_i^2}{c^2} \bar{\epsilon} \cdot \bar{E}(\bar{r}, \omega_i) = 4\pi \frac{\omega_i^2}{c^2} \bar{P}^{NL}(\bar{r}, \omega_i) \quad (7.76)$$

where $i=1$ (pump), 2 (Stokes), 3 (anti-Stokes) or 4 (second order Stokes). To account for the small dispersion effects in gases, the

index of refraction at ω_i , n_i may be introduced so that $n_i^2 = |\epsilon|$. A second useful equation is that obtained from Eq (2.2a) and (2.15d) such that

$$\nabla \cdot (\bar{\epsilon} \cdot \bar{E})(\bar{r}, \omega_i) = -4\pi \nabla \cdot \bar{P}^{NL}(\bar{r}, \omega_i) \quad (7.77)$$

In many approaches to solving the wave equation the variation of \bar{P}^{NL} in Eq (7.77) is assumed to be negligible and $\bar{\epsilon}$ is assumed to be isotropic so that

$$\nabla \cdot \bar{E}(\bar{r}, \omega_i) = 0 \quad (7.78)$$

Using this with the vector identity

$$\nabla \times \nabla \times \bar{E} = \nabla^2 \bar{E} - \nabla (\nabla \cdot \bar{E}) \quad (7.79)$$

simplifies the wave equation.

Any solution to the set of Eqs (7.76) and (7.77) must satisfy certain conditions. Two conditions that must be satisfied are the conservation of energy and conservation of momentum. For well defined frequencies and propagation vectors, these may be written as

$$\sum_{i=1}^4 \omega_i = 0 \quad (7.80)$$

$$\sum_{i=1}^4 \bar{k}_i = 0 \quad (7.81)$$

respectively, and where

$$|\bar{k}_i| = \frac{n_i \omega_i}{c} \quad (7.82)$$

The boundary conditions of Eq (2.6) must also be satisfied at any

boundary. Where there is a second beam incident on the boundary as is being considered here, the components of k satisfying the boundary conditions are determined at the boundary (Ref 25:117). Any propagation phase mismatch, Δk , is also determined. In principle then, it is possible to solve the wave equation for the fields using these equations and nonlinear polarizations. This is an extremely difficult task even with the use of numerical techniques since the results are a set of twelve coupled, second order, nonlinear partial differential equations.

Several simplifying assumptions have been developed to reduce the task of solving the set of equations for the electric fields. One assumption most commonly accepted is that of slowly varying amplitude. This assumption is valid when the change in amplitude of a wave per wavelength is small. This occurs because the nonlinear susceptibility is a very small quantity compared to the linear one ($x^{(1)} : x^{(3)} \sim 1 : 10^{-14}$ (Ref 72:119)). The result is that the second derivative of amplitude is negligible (Ref 26:1958) i.e.,

$$\frac{\partial^2 A}{\partial z^2} \ll k \frac{\partial A}{\partial z} \quad (7.83)$$

and the set of coupled equations become first order partial differential equations. A second assumption commonly used is that the solution has the form of a plane wave

$$\bar{E}(\bar{r},t) = \bar{A}(\bar{r}) e^{i(\bar{k} \cdot \bar{r} - \omega t)} \quad (7.84)$$

or a Gaussian spherical wave

$$\bar{E}(\bar{r},t) = \bar{A}(\bar{r}) e^{-(\alpha+i\beta)\rho^2} e^{i(\bar{k} \cdot \bar{r} - \omega t)} \quad (7.85)$$

where the amplitude term, $A(\bar{r})$, may be complex. Equation (7.85) is that characteristic of the wave generated by a laser source.

Bjorklund (Ref 105:288) has proposed a specific and therefore more useful form for the field propagating along the z axis.

If additional assumptions are made on the strength of interaction of the fields, analytic solutions can be obtained. Bloembergen (Ref 25:110) by assuming the pump field, E_1 , to remain unchanged and the fields to be in the form of monochromatic plane waves solves the coupled equations of the Stokes and anti-Stokes fields for SRS-S and CARS processes included. This case is the least restrictive one that can be solved analytically. To further simplify the problem, the pump field and Stokes field can be assumed to remain unchanged during the interaction; the weak interaction condition. When this assumption is made along with those of slowly varying amplitudes, plane waves, and parallel field polarizations, the anti-Stokes intensity in the CARS process may be obtained directly for the multifrequency case as (Ref 86:9)

$$I_3(\omega_3 + \delta) = \left(\frac{4\pi^2 \omega_3}{n^2 c^2} \right)^2 I_1^2 I_2(\omega_2 - \delta) | 3x_{1111}^{\text{CARS}} (-\omega_3 - \delta; -\omega_2 - \delta, \omega_1, \omega_1) |^2 \\ \times L^2 [\sin(x)/x]^2 \quad (7.86)$$

where

L = interaction length

$x = \Delta k L/2$

$\Delta k = |\bar{k}_1 + \bar{k}_1 - \bar{k}_2 - \bar{k}_3| = \text{phase mismatch}$

Equation (7.86) shows the effect of phase mismatch on the anti-Stokes intensity. Weil and Schreiber (Ref 106) have numerically solved the coupled set of equations for the four fields being considered here and have included most of the six nonlinear processes. The following assumptions are made in the solutions of Weil and Schreiber; vibrational transitions only, slowly varying amplitudes, monochromatic plane waves, parallel polarization and a variable state population. The assumption of slowly varying amplitudes was checked and found to hold for the input conditions used. The inclusion of the rate of change in population of the various states was a valuable improvement.

State Population. The solution of the wave equation with the correct boundary conditions provides the description of fields. The key to the correct formulation of these equations is the nonlinear third order polarization. It serves as the forcing function of the particular solution. From the results obtained for this polarization, the corresponding set of susceptibilities are directly dependent on the population in the various molecular states involved in a given process. When no electronic resonance enhancement is present, the dependence is on the difference between the population of the two involved states. If this difference becomes zero, the susceptibility will also be zero. The density difference is in turn dependent on the fields or intensity generated by the processes. Thus, the equation describing the rate of change of the density or density difference is coupled to the set of field equations.

Maier, et.al. (Ref 85:582) derive an expression for the equation of motion of the population difference density for a two-level system involved in the SRS process. This derivation, based upon a harmonic

oscillator model, relates the rate of change of the difference in probability of finding the molecule in each state to the first derivative of the polarizability and the molecular vibrational displacement. In this form, the result is only a guide to one for this work. Druet, et.al. (Refs 97:1546 and 107:20) have used the equation of motion of the density operator and perturbation theory to obtain a rate equation for the probability of population difference for both electronic resonance enhancement (with $\rho_{11}^0 = 0$) and no electronic resonance enhancement. The equation obtained accounts for the SRS-S, SRS-P and CARS process. It is necessary, however, as pointed out, to explicitly write out the all fields. This was done assuming monochromatic plane waves. The equation for off resonance is fairly compact while the one for electronic resonance is very complex. Weil and Schreiber (Ref 106:944) have used a more straightforward approach of equating the rate of change of the population difference to the increase in the photon density due to an SRS process over a differential path length. This is in turn related to the rate of increase in the field over the same path length. These equations are given for both a two level and a three level system with damping phenomenologically added.

The results of Druet, if extended to all of the processes considered here, is a more complete description of the change in the population difference. However, the approach by Weil lends itself very readily to numerical calculations as demonstrated and is easily adapted to multilevel systems. Further efforts in determining the best population difference rate equation are needed for the general case under consideration in this research.

Linewidth. The linewidth is a parameter that occurs in every Raman resonance susceptibility and becomes dominant in the denominator when resonance is reached. An understanding of the linewidth and hence the line shape is important whether CARS is being used to measure macroscopic parameters or study molecular properties. The linewidth is a superposition of the natural width with the physical phenomena of molecular motion and intermolecular collisions. The effect of the processes vary with the density of the gas. At low densities where collisions are infrequent, the Doppler effect of the molecular motion is superimposed on the natural line width. As the pressure increases and the collision frequency also increases Dicke narrowing (Ref 108) of the Doppler linewidth can occur. The appearance of Dicke narrowing depends on the magnitude of the Doppler broadening and the onset of pressure broadening. As the density is further increased, the collisional effects dominate and collisional broadening of the line is observed. With still further increase in the density, a region of fairly constant linewidth is reached and then the linewidth decreases with density (e.g., collisional narrowing occurs at about 30 amagats in nitrogen (Ref 109)). Not only does the linewidth change with density, but the shape is also changed and the rotational-vibrational energy is shifted.

At low density where the Doppler effects dominate, linewidth is approximately constant. Roh, et.al (Ref 110) derived an expression for the Doppler effect on linewidth in the forward scattering direction of

$$\text{CARS } x_{1111}(\omega) = K_j \cdot \left(\frac{(4/\pi) \ln 2}{\Delta\omega_D^{-2}} \right)^{1/2} \int_{-\infty}^{\infty} \frac{d\xi}{\omega - j\xi - \omega - i\Gamma} e^{(-4(\ln 2)\xi^2/\Delta\omega_D^{-2})} \quad (7.87)$$

where

$\Delta\omega'_D$ = Doppler width (fwhm) for forward Raman scattering

$\zeta = (nv/c) \omega_j'$ = Doppler shift in the resonant frequency

Based upon Eq (7.87), it was concluded that the anti-Stokes intensity would have a Gaussian profile with a linewidth (fwhm) of $1.22 \Delta\omega'_D$ so that the CARS linewidth is broader than that for forward scattered Raman by a factor 1.22. However, when collisional broadening occurs $\Gamma = \Gamma_n + \Gamma_p \gg \Delta\omega'_D$, the shape is given by a Lorentzian with linewidth of 2Γ . In the intermediate density case, when Dicke narrowing occurs, the effect on the susceptibility has been obtained using the autocorrelation function of the scattered field (Ref 111:178).

A theory for high pressure CARS spectra where collisional narrowing occurs, has been developed by Hall (Ref 112 and 113). This theory treats the prediction of Γ for the regions where collisional broadening occurs and the linewidth is found to be proportional to the pressure and temperature as

$$\Gamma_t = \Gamma_T p T^{-\frac{1}{2}} \quad (7.88)$$

where

Γ_t = linewidth at any pressure and temperature

Γ_T = known linewidth at a given pressure and temperature

In the region where collisional narrowing occurs, the dependence on density is a complex function and no longer linear. However, when the density gets sufficiently high that the narrowing ceases and the linewidth again becomes approximately constant, it again becomes a

weak linear function of the density.

The linewidth is also a function of the initial rotational level associated with the Raman transition. Data for this variation for Raman scattering (N_2 and CO_2) (Ref 114:187-188) and CARS (N_2) (Ref 115) are available. CARS data were compared to the Bonamy theory by Hall (Ref 112) and found to give excellent agreement with respect to both J value and temperature. This theory is predictive in the sense that no adjustable parameters are needed for the calculation and can be extended for use with several diatomic molecules.

There are additional effects that can change the linewidth or line shape. Three sources of these effects are the measurement being made, the method of measurement and the laser source being used. In terms of the laser measurement, if the integrated intensity is measured by using a multifrequency (broad band) Stokes beam with a near monochromatic pump (Ref 86:16) there is an effective line width due to the interaction of the Raman resonance susceptibility, off resonance susceptibility and the electronic non-resonant susceptibility. This Γ_{eff} results in a reduction of the linewidth parameter used with the integrated intensity. The effect of laser source is treated by Yuratich (Ref 116) by considering the effect of incoherence in the source to reduce the equation of the anti-Stokes spectral intensity to a convolution over laser lineshapes. The results are presented in tabular form summarizing the requirement on the laser linewidth and resonant frequency difference necessary for the spectra obtained to follow the Raman anti-Stokes spectrum.

VIII. Summary, Recommendations and Conclusions

Summary

The results of this research are a set of third order polarization equations that completely describe the nonlinear CARS and related processes in gases. The form of the equations is appropriately macroscopic for interpretation of experimental results. The molecular gas polarizations derived are correct for all electric field vector polarizations and any nonoverlapping frequency distribution of the electric field amplitude. The derivation does assume two laser input beams whose central frequencies are separated by a Raman rotational-vibrational resonance frequency and two generated beams whose central frequency is shifted from the two input beams positively and negatively by the same resonance frequency. In order to describe the CARS completely, five other nonlinear processes, two parametric (CSRS and CMRS) and three nonparametric (SRS-S, P, and SS), that depend on these four fields are included.

A semiclassical approach with the electromagnetic field described classically is used in the polarization derivation. Both classical and fully quantized excursions are made where they contribute to the understanding or clarity of the resulting equations. Specifically, the induced third order molecular polarizability is obtained from quantum mechanical perturbation theory using a density operator. This polarizability along with the electric fields defines the dipole moment of the molecule. The dipole moment is divided into two parts; one possessing a resonant denominator for a Raman transition and one that represents nonresonant terms. Since the medium polarization is

an orientational average of the molecular dipole moments, the resonant part is averaged for a gas having a random orientation. The result of this averaging when combined with the nonresonant term is the medium polarization. The medium polarization is defined by the set of equations for each of the six processes and the four central frequencies.

From the equations for the medium polarization, macroscopic susceptibilities are defined (Appendix J) that depend on pseudo polarizability invariants. These pseudo invariants are shown to have the same form as the Raman polarizability invariants. In the absence of electronic resonances, dispersion in the polarizability is small so that the third order polarizability invariants can be set equal to products of the Raman polarizability invariants. By carefully deriving the molecular Raman differential scattering cross section and establishing the dependence of the average Raman cross section on the same Raman polarizability invariants, the conditions under which the various susceptibilities are related to the correct Raman scattering cross section are presented. A discussion of important parameters, scaling and the field solutions is given for completeness. The objective of obtaining the medium polarization and the defining susceptibilities that describe CARS in terms of measurable parameters was accomplished.

Recommendations

The equations for linewidth and the rate of change in population density should be determined. This would include the effect of laser lineshape (Ref 116). These equations should account for all of the

processes considered in this research and should have as parameters factors that can be obtained from other experiments. This would provide a complete and consistent set of equations to predict and interpret the CARS process. The available set of equations can then be solved to determine the effect of secondary nonlinear processes, phase matching and field polarization on the generation of a CARS field. An extension of the set of equations to include nondegenerate four wave mixing is straight-forward and should be carried out for completeness. A more difficult but more significant extension of the research would be to determine the role of the polarizability and pseudo polarizability invariants for electronic resonance enhancement. The scaling of the antisymmetric invariant must also be established. Any effect of the antisymmetric invariant and its magnitude should be experimentally determined. This is especially true for electronic resonance enhancement. The magnitude of the pseudo polarizability invariants variation with frequency also needs to be established by experiment. This would determine the degree of accuracy in equating the Raman polarizability invariants to the pseudo invariants. The scaling of the pseudo invariants with vibrational and rotational levels should also be experimentally verified.

Conclusions

The third order polarization equations obtained in this research for the description of CARS are complete and unambiguous. Further, they form a set of equations that can be used to solve for the CARS electric fields as well as those of the other processes with any form of the laser source; monochromatic or multifrequency. The general

results obtained here do reduce to the accepted simpler monochromatic equations. Coherence properties of the laser sources have not, however, been included in this analysis. By retaining the arbitrariness of the input fields, the susceptibilities determining the medium polarization are seen to depend on terms that combine and therefore disappear when the monochromatic assumption is made. For example, the two different denominator terms in the CARS(1) susceptibility is not generally recognized. Also, several authors have proposed relationships between the various susceptibilities that in reality only apply under certain restrictive assumptions. Others have taken the susceptibility for a gas to be the form of the molecular polarizability. This is at best confusing to someone new to this field and may result in application errors. This error is corrected by the approach presented here. By using the set of susceptibility equations derived, within the assumptions made, each constant and coefficient is carefully defined and the differences in the susceptibility expressions appearing in the literature are eliminated. The equations derived here, where appropriate, or the approach for other situations specifies clearly the conditions under which the susceptibility terms can be replaced by Raman cross sections. The correct cross section to be used is also clearly specified.

The results obtained here for arbitrary electric field polarization is also presented for the first time. Yuratich (Ref 104) has derived a scalar susceptibility that for certain conditions accurately describes the relation between susceptibility components. But, in general, because his result is in scalar form, the vector information

of each polarization component cannot be uniquely stated. The form of the polarization equations derived herein being expressed in the laboratory coordinate system makes it very easy to visualize and understand the role played by each polarization vector component. This can be important in such applications as background suppression. The results stated by Oudar (Ref 100) and Eckbreth (Ref 98) are easily derived from the equations of this research and the impact of other terms is easily seen. Although the derivation performed here was for degenerate four wave mixing (two of the three input frequencies are identical), the approach is applicable to the case of a third input beam frequency with different polarization. The results are therefore easily extended to such applications as the Asterisk method of background suppression. This approach is also applicable to examining the case of electronic resonance enhancement. In the use of this set of polarization equations, existing experimental data may be used for the simpler cases. For these more complicated applications, the required data must first be experimentally obtained.

In conclusion, the set of equations derived here are not only unique in their completeness in describing the macroscopic third order medium polarization and susceptibilities, but, the approach is broad in its applicability as well as being straight forward. This approach is quite clear in distinguishing between the susceptibility which is macroscopic and the polarizability which is molecular in nature. This can be significant in the correct interpretation of experimental results.

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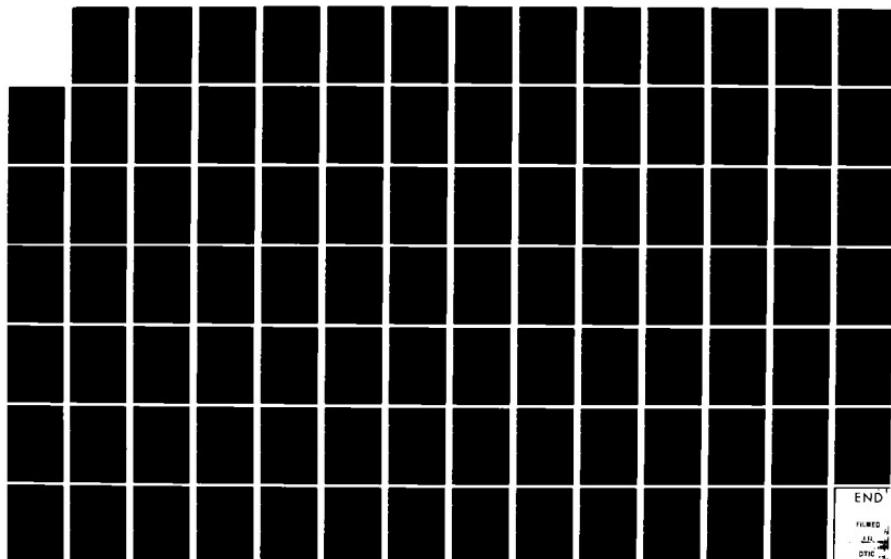
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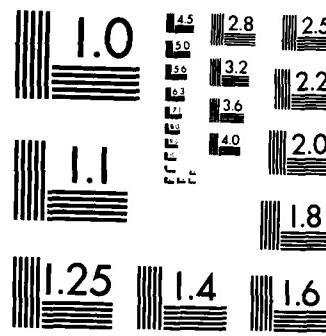
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Appendix A: Medium Susceptibility

The form of the various orders of the susceptibility, Eq (2.13), relating the higher order polarization terms of Eq (2.11) to the applied fields is essential to the development of CARS as a diagnostic tool. Following the approach of Butcher (Ref 48), the general form of the third order susceptibility is derived with minimum assumptions. One very useful property, the intrinsic permutation symmetry, is shown to be a result of the general functional relationship.

A general expression that can be written between the time dependent vectors $\bar{P}(t)$ and $\bar{E}(t)$ is

$$\bar{P}^{(1)}(t) = \int_{-\infty}^{\infty} d\tau \quad \bar{Q}^{(1)}(t, \tau) \cdot \bar{E}(\tau) \quad (A1)$$

$$\bar{P}^{(2)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \quad \bar{Q}^{(2)}(t, \tau_1, \tau_2) : \bar{E}(\tau_1) \bar{E}(\tau_2) \quad (A2)$$

$$\bar{P}^{(3)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \quad \bar{Q}^{(3)}(t, \tau_1, \tau_2, \tau_3) : \bar{E}(\tau_1) \bar{E}(\tau_2) \bar{E}(\tau_3) \quad (A3)$$

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These may be written in component form as

$$p_{\mu}^{(1)}(t) = \int_{-\infty}^{\infty} d\tau \quad Q_{\mu\alpha}^{(1)}(t, \tau) E_{\alpha}(\tau) \quad (A1a)$$

$$p_{\mu}^{(2)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \quad Q_{\mu\alpha_1\alpha_2}^{(2)}(t, \tau_1, \tau_2) E_{\alpha_1}(\tau_1) E_{\alpha_2}(\tau_2) \quad (A2a)$$

$$p_{\mu}^{(3)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \\ \times \quad Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(t, \tau_1, \tau_2, \tau_3) E_{\alpha_1}(\tau_1) E_{\alpha_2}(\tau_2) E_{\alpha_3}(\tau_3) \quad (A3a)$$

From this form it is clear that $\bar{Q}^{(i)}$ is a tensor of rank $i + 1$. Here,

as throughout this work, the subindices represent spatial coordinates and the Einstein convention that repeated indices represent sums is used, as defined by Eq (3.15).

By using the properties of time displacement and time invariance, it can be shown that \bar{Q} depends only upon the difference of two times. This can be shown for all orders of Q by demonstrating it on $\bar{Q}^{(3)}$ which is of prime interest in this study. First applying time displacement let $t \rightarrow t + T$ in Eq (A3a).

$$P_{\mu}^{(3)}(t+T) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \\ \times Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(t+T, \tau_1, \tau_2, \tau_3) E_{\alpha_1}(\tau_1) E_{\alpha_2}(\tau_2) E_{\alpha_3}(\tau_3) \quad (A4)$$

Also, with the assumption of time invariance, $P_{\mu}^{(3)}(t+T)$ must depend on $E(t+T)$. Equation (A3a) becomes

$$P_{\mu}^{(3)}(t+T) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \\ \times Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(t, \tau_1, \tau_2, \tau_3) E_{\alpha_1}(\tau_1+T) E_{\alpha_2}(\tau_2+T) E_{\alpha_3}(\tau_3+T) \quad (A5)$$

Upon making the change of variables $\tau_1+T \rightarrow \tau_1$, $\tau_2+T \rightarrow \tau_2$ and $\tau_3+T \rightarrow \tau_3$

$$P_{\mu}^{(3)}(t+T) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \\ \times Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(t, \tau_1-T, \tau_2-T, \tau_3-T) E_{\alpha_1}(\tau_1) E_{\alpha_2}(\tau_2) E_{\alpha_3}(\tau_3) \quad (A6)$$

Comparing Eqs (A4) and (A6) it can be seen that

$$Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(t+T, \tau_1, \tau_2, \tau_3) = Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(t, \tau_1-T, \tau_2-T, \tau_3-T)$$

must hold. Since this is true for any t , T or τ set $t = 0$ and $T = t$.

$$Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(t, \tau_1, \tau_2, \tau_3) = Q_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(0, \tau_1-t, \tau_2-t, \tau_3-t)$$

Thus $\bar{Q}^{(3)}$ depends on the time difference and not on absolute values of time. For definiteness let

$$\bar{Q}^{(3)}(t, \tau_1, \tau_2, \tau_3) = \bar{R}^{(3)}(t-\tau_1, t-\tau_2, t-\tau_3) \quad (A7)$$

Thus Eq (A3a) becomes

$$\bar{P}^{(3)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \bar{R}^{(3)}(t-\tau_1, t-\tau_2, t-\tau_3) : \bar{E}(\tau_1) \bar{E}(\tau_2) \bar{E}(\tau_3) \quad (A8a)$$

or

$$\bar{P}^{(3)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \bar{R}^{(3)}(\tau_1, \tau_2, \tau_3) : \bar{E}(t-\tau_1) \bar{E}(t-\tau_2) \bar{E}(t-\tau_3) \quad (A8b)$$

In Eq (A8b), a change of variable under the integral has been used.

$\bar{R}^{(3)}(\tau_1, \tau_2, \tau_3)$ is the cubic (third order) polarization response function of the medium.

Two additional assumptions are appropriate for the conditions encountered; causality and reality. The causality condition requires that $\bar{P}^{(3)}(t)$ not depend on the value of fields later than t (i.e., $\tau < t$). To incorporate this assumption, $\bar{R}^{(3)}$ is defined as

$$\bar{R}^{(3)}(\tau_1, \tau_2, \tau_3) = \mathbb{H}(\tau_1) \mathbb{H}(\tau_2) \mathbb{H}(\tau_3) \bar{R}^{(3)}(\tau_1, \tau_2, \tau_3)$$

where

$$\mathbb{H}(\tau) = \begin{cases} 0 & \tau < 0 \\ 1 & \tau \geq 0 \end{cases}$$

The reality conditions requires that $\bar{P}^{(3)}(t)$ be real when $\bar{E}(t)$ is real. This requires that $\bar{R}^{(3)}(\tau_1, \tau_2, \tau_3)$ be real also.

There is a permutation symmetry of $\bar{R}^{(3)}$ associated with the form of the relation between $\bar{P}^{(3)}$ and \bar{E} in Eq (A8). This property is very useful in the manipulation of variables and is called the intrinsic permutation symmetry. This property provides for $R_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\tau_1, \tau_2, \tau_3)$ to be invariant under the $3!$ permutations of the pairs $\alpha_1\tau_1$, $\alpha_2\tau_2$ and $\alpha_3\tau_3$. That this property follows from the form of the equation for any order r of the polarization will be shown for the case of $r=3$. Starting with Eq (A8b) written in component form

$$P_{\mu}^{(3)}(t) = \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 R_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\tau_1, \tau_2, \tau_3) E_{\alpha_1}(\tau_1) E_{\alpha_2}(\tau_2) E_{\alpha_3}(\tau_3) \quad (A9)$$

where the t dependence of E has been suppressed for convenience. Upon examination of specific combinations of the 27 terms and 6 permutations, it is possible to show that the intrinsic permutation symmetry holds. The term $R_{\mu 111}^{(3)}(\tau_1, \tau_2, \tau_3)$ is used as an example of the three terms where $\alpha_1 = \alpha_2 = \alpha_3$

$$\int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 R_{\mu 111}^{(3)}(\tau_1, \tau_2, \tau_3) E_1(\tau_1) E_1(\tau_2) E_1(\tau_3) \quad (A10)$$

For this, consider an $\bar{R}^{(3)}$ term whose first two pairs, $1\tau_1$ and $1\tau_2$ are interchanged:

$$\int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 R_{\mu 111}^{(3)}(\tau_2, \tau_1, \tau_3) E_1(\tau_1) E_1(\tau_2) E_1(\tau_3) \quad (A11)$$

However, τ_1 and τ_2 are dummy variables of integration so that without loss of generality the change of variables can be made

$$\tau_1 \rightarrow \tau_2; d\tau_1 \rightarrow d\tau_2$$

$$\tau_2 \rightarrow \tau_1; d\tau_2 \rightarrow d\tau_1$$

and Eq (A11) becomes

$$\iiint_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 R_{\mu 111}^{(3)}(\tau_1, \tau_2, \tau_3) E_1(\tau_2) E_1(\tau_1) E_1(\tau_3) \quad (A12)$$

Since E_1 is a scalar, it may be rearranged

$$\iiint_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 R_{\mu 111}^{(3)}(\tau_1, \tau_2, \tau_3) E_1(\tau_1) E_1(\tau_2) E_1(\tau_3) \quad (A13)$$

After setting Eq (A11) equal to Eq (A13) collect terms to the right hand side. This procedure yields

$$\begin{aligned} & \iiint_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 [R_{\mu 111}^{(3)}(\tau_2, \tau_1, \tau_3) \\ & - R_{\mu 111}^{(3)}(\tau_1, \tau_2, \tau_3)] E_1(\tau_1) E_1(\tau_2) E_1(\tau_3) = 0 \end{aligned} \quad (A14)$$

The electric field product in Eq (A14) is arbitrary so that the only way equality can hold in general is for the coefficient of the field product to be zero.

$$R_{\mu 111}^{(3)}(\tau_2, \tau_1, \tau_3) - R_{\mu 111}^{(3)}(\tau_1, \tau_2, \tau_3) = 0$$

or

$$R_{\mu 111}^{(3)}(\tau_2, \tau_1, \tau_3) = R_{\mu 111}^{(3)}(\tau_1, \tau_2, \tau_3) \quad (A15)$$

By straightforward examination, this must be true independent of the permutation and thus is also true for the other five permutations and for $R_{\mu 222}^{(3)}$ and $R_{\mu 333}^{(3)}$.

Now consider the case where the indices on $R_{\mu}^{(3)}$ are all different, for example

$$\begin{aligned}
& \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \left[R_{\mu 123}^{(3)} (\tau_1, \tau_2, \tau_3) E_1(\tau_1) E_2(\tau_2) E_3(\tau_3) \right. \\
& + R_{\mu 213}^{(3)} (\tau_1, \tau_2, \tau_3) E_2(\tau_1) E_1(\tau_2) E_3(\tau_3) \\
& + R_{\mu 231}^{(3)} (\tau_1, \tau_2, \tau_3) E_2(\tau_1) E_3(\tau_2) E_1(\tau_3) \\
& + R_{\mu 132}^{(3)} (\tau_1, \tau_2, \tau_3) E_1(\tau_1) E_3(\tau_2) E_2(\tau_3) \\
& + R_{\mu 312}^{(3)} (\tau_1, \tau_2, \tau_3) E_3(\tau_1) E_1(\tau_2) E_2(\tau_3) \\
& \left. + R_{\mu 321}^{(3)} (\tau_1, \tau_2, \tau_3) E_3(\tau_1) E_2(\tau_2) E_1(\tau_3) \right] \quad (A16)
\end{aligned}$$

Interchange the first two pairs in $R_{\mu}^{(3)}$ as before with τ_1 replaced by 1, etc., for convenience

$$\begin{aligned}
& \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \left[R_{\mu 213}^{(3)} (2, 1, 3) E_1(1) E_2(2) E_3(3) + R_{\mu 123}^{(3)} (2, 1, 3) E_2(1) E_1(2) E_3(3) \right. \\
& + R_{\mu 321}^{(3)} (2, 1, 3) E_2(1) E_3(2) E_1(3) + R_{\mu 312}^{(3)} (2, 1, 3) E_1(1) E_3(2) E_2(3) \\
& \left. + R_{\mu 132}^{(3)} (2, 1, 3) E_3(1) E_1(2) E_2(3) + R_{\mu 231}^{(3)} (2, 1, 3) E_3(1) E_2(2) E_1(3) \right] \quad (A17)
\end{aligned}$$

When the variable of integration property is used to interchange τ_1 and τ_2 in Eq (A17), it becomes

$$\begin{aligned}
& \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \left[R_{\mu 213}^{(3)} (1, 2, 3) E_1(2) E_2(1) E_3(3) + R_{\mu 123}^{(3)} (1, 2, 3) E_2(2) E_1(1) E_3(3) \right. \\
& + R_{\mu 321}^{(3)} (1, 2, 3) E_2(2) E_3(1) E_1(3) + R_{\mu 312}^{(3)} (1, 2, 3) E_1(2) E_3(1) E_2(3) \\
& \left. + R_{\mu 132}^{(3)} (1, 2, 3) E_3(2) E_1(1) E_2(3) + R_{\mu 231}^{(3)} (1, 2, 3) E_3(2) E_2(1) E_1(3) \right] \quad (A18)
\end{aligned}$$

The scalar property of the electric field component product provides that Eq (A18) becomes

$$\begin{aligned} \int_{-\infty}^{\infty} \int d_1 \int d_2 \int d_3 & \left[R_{\mu_{123}}^{(3)}(1,2,3)E_1(1)E_2(2)E_3(3) + R_{\mu_{213}}^{(1)}(1,2,3)E_2(1)E_1(2)E_3(3) \right. \\ & + R_{\mu_{231}}^{(3)}(1,2,3)E_2(1)E_3(2)E_1(3) + R_{\mu_{132}}^{(3)}(1,2,3)E_1(1)E_3(2)E_2(3) \\ & \left. + R_{\mu_{312}}^{(3)}(1,2,3)E_3(1)E_1(2)E_2(3) + R_{\mu_{321}}^{(3)}(1,2,3)E_3(1)E_2(2)E_1(3) \right] \quad (A19) \end{aligned}$$

This is exactly Eq (A16). Collect terms to the right hand side after equating Eqs (A17) and (A19).

$$\begin{aligned} \int_{-\infty}^{\infty} \int d_1 \int d_2 \int d_3 & \left\{ \left[R_{\mu_{213}}^{(3)}(2,1,3) - R_{\mu_{123}}^{(3)}(1,2,3) \right] E_1(1)E_2(2)E_3(3) \right. \\ & + \left[R_{\mu_{123}}^{(3)}(2,1,3) - R_{\mu_{213}}^{(3)}(1,2,3) \right] E_1(2)E_2(1)E_3(3) \\ & + \left[R_{\mu_{321}}^{(3)}(2,1,3) - R_{\mu_{231}}^{(3)}(1,2,3) \right] E_1(3)E_2(1)E_3(2) \\ & + \left[R_{\mu_{312}}^{(3)}(2,1,3) - R_{\mu_{132}}^{(3)}(1,2,3) \right] E_1(1)E_2(3)E_3(2) \\ & + \left[R_{\mu_{132}}^{(1)}(2,1,3) - R_{\mu_{312}}^{(1)}(1,2,3) \right] E_1(2)E_2(3)E_3(1) \\ & \left. + \left[R_{\mu_{231}}^{(3)}(2,1,3) - R_{\mu_{321}}^{(3)}(1,2,3) \right] E_1(3)E_2(2)E_3(1) \right\} = 0 \quad (A20) \end{aligned}$$

But, again the electric fields are arbitrary so that the only way for equality to hold without loss of generality is for the individual coefficients of the fields to be zero.

$$R_{\mu_{213}}^{(3)}(2,1,3) - R_{\mu_{123}}^{(3)}(1,2,3) = 0 \rightarrow R_{\mu_{123}}^{(3)}(1,2,3) = R_{\mu_{213}}^{(3)}(2,1,3)$$

$$R_{\mu_{123}}^{(3)}(2,1,3) - R_{\mu_{213}}^{(3)}(1,2,3) = 0 \rightarrow R_{\mu_{213}}^{(3)}(1,2,3) = R_{\mu_{123}}^{(3)}(2,1,3)$$

$$R_{\mu_{321}}^{(3)}(2,1,3) - R_{\mu_{231}}^{(3)}(1,2,3) = 0 \rightarrow R_{\mu_{231}}^{(3)}(1,2,3) = R_{\mu_{321}}^{(3)}(2,1,3)$$

$$R_{\mu_{312}}^{(3)}(2,1,3) - R_{\mu_{132}}^{(3)}(1,2,3) = 0 \rightarrow R_{\mu_{132}}^{(3)}(1,2,3) = R_{\mu_{312}}^{(3)}(2,1,3)$$

$$R_{\mu_{132}}^{(3)}(2,1,3) - R_{\mu_{312}}^{(3)}(1,2,3) = 0 \rightarrow R_{\mu_{312}}^{(3)}(1,2,3) = R_{\mu_{132}}^{(3)}(2,1,3)$$

$$R_{\mu_{231}}^{(3)}(2,1,3) - R_{\mu_{321}}^{(3)}(1,2,3) = 0 \rightarrow R_{\mu_{321}}^{(3)}(1,2,3) = R_{\mu_{231}}^{(3)}(2,1,3) \quad (A21)$$

By repeating this process, it can be shown that the invariance holds under the other five pair permutations possible. Further, by treating the case where two of the indices are the same (e.g., 112) in the same manner the invariance property can be shown to hold for all of the components (e.g.,

$$R_{\mu_{112}}^{(3)}(1,2,3) = R_{\mu_{121}}^{(3)}(1,3,2), R_{\mu_{121}}^{(3)}(1,2,3) = R_{\mu_{112}}^{(3)}(1,3,2),$$

$$R_{\mu_{211}}^{(3)}(1,2,3) = R_{\mu_{211}}^{(3)}(1,3,2), \text{ etc.})$$

This proves that the intrinsic permutation symmetry holds for all 27 components of $R_{\mu_{\alpha_1\alpha_2\alpha_3}}^{(3)}$ associated with the index pairs $\alpha_1^\tau, \alpha_2^\tau$, α_3^τ and is a property of the form of the relation between \bar{P} and \bar{E} . This symmetry is also independent of the order.

With the properties stated, the relationship between the polarization response tensor and the susceptibility tensor can be obtained. The susceptibility tensor is that function that relates the medium polarization, \bar{P} , to the electric field, \bar{E} , when the field vector is expressed as a function of the frequency, ω rather than time. This

transformation to frequency dependence is obtained using Fourier transforms:

$$E'(t) = \int_{-\infty}^{\infty} E(\omega) e^{-i\omega t} \quad (a)$$

$$E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} E'(t) e^{i\omega t} \quad (b) \quad (A22)$$

In keeping with Butcher (Ref 48:15) ω may lie in the upper-half complex plane such that $\omega = \omega' + i\omega''$ with ω' and ω'' real and $\omega'' > 0$. The integral for $E(\omega)$ in Eq (A22) will converge under these conditions provided that $\lim_{t \rightarrow -\infty} E(t) \rightarrow 0$. Equation (A22a) substituted into Eq (A8b) yields

$$\bar{P}^{(3)}(t) = \iiint_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \bar{R}^{(3)}(\tau_1, \tau_2, \tau_3) \bar{E}'(t - \tau_1) \bar{E}'(t - \tau_2) \bar{E}'(t - \tau_3) \quad (A23)$$

where

$$\bar{E}'(t - \tau_i) = \int_{-\infty}^{\infty} d\omega_i \bar{E}(\omega_i) e^{-i\omega_i(t - \tau_i)}$$

Or

$$\begin{aligned} \bar{P}^{(3)}(t) = & \iiint_{-\infty}^{\infty} d\omega_1 d\omega_2 d\omega_3 \left[\iiint_{-\infty}^{\infty} d\tau_1 d\tau_2 d\tau_3 \bar{R}^{(3)}(\tau_1, \tau_2, \tau_3) \right. \\ & \times e^{i(\omega_1 \tau_1 + \omega_2 \tau_2 + \omega_3 \tau_3)} \left. : \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3) e^{-i(\omega_1 + \omega_2 + \omega_3)t} \right] \end{aligned} \quad (A24)$$

For $\bar{x}^{(3)}$ set equal to the Fourier transform of the response function

$$\bar{x}^{(3)}(\omega_1, \omega_2, \omega_3) \equiv \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_3 \bar{R}(\tau_1, \tau_2, \tau_3) e^{i(\omega_1 \tau_1 + \omega_2 \tau_2 + \omega_3 \tau_3)} \quad (A25)$$

where $\bar{x}^{(3)}$ is defined as the third order susceptibility. Then

Eq (A24) becomes

$$\bar{p}^{(3)}(t) = \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \bar{x}^{(3)}(\omega_1, \omega_2, \omega_3) \cdot \bar{E}(\omega_1) \bar{E}(\omega_2) \bar{E}(\omega_3) \\ \times e^{-i(\omega_1 + \omega_2 + \omega_3)t} \quad (A26)$$

The spatial dependence is present but has been suppressed for convenience.

The conditions imposed by causality, reality and symmetry on the third order susceptibility are (Ref 48:17)

(1) Causality. $\bar{x}^{(3)}(\omega_1, \omega_2, \omega_3)$ is analytic for ω_1 , ω_2 , and ω_3 in the upper-half plane.

$$(2) \text{ Reality. } \left[\bar{x}^{(3)}(\omega_1, \omega_2, \omega_3) \right]^* = \bar{x}^{(3)}(-\omega_1^*, -\omega_2^*, -\omega_3^*)$$

(3) Symmetry. $x_{\mu\alpha\beta\gamma}^{(3)}(\omega_1, \omega_2, \omega_3)$ is invariant under the $3!$ permutations of the pairs (α, ω_1) , (β, ω_2) and (γ, ω_3)

$$(\text{i.e., } x_{\mu\alpha\beta\gamma}^{(3)}(\omega_1, \omega_2, \omega_3) = x_{\mu\beta\alpha\gamma}^{(3)}(\omega_2, \omega_1, \omega_3) = x_{\mu\gamma\beta\alpha}^{(3)}(\omega_3, \omega_2, \omega_1) \\ = x_{\mu\alpha\gamma\beta}^{(3)}(\omega_1, \omega_3, \omega_2) = x_{\mu\beta\gamma\alpha}^{(3)}(\omega_2, \omega_3, \omega_1) = x_{\mu\gamma\alpha\beta}^{(3)}(\omega_3, \omega_1, \omega_2))$$

The first order and second order susceptibilities in terms of the respective response functions are obtained by Butcher (Ref 48:12-16). The form of the general order n is also presented in this reference.

Appendix B: Density Operator

The density operator, $\hat{\rho}(\vec{r},t)$, or equivalently a density matrix representation is the quantum equivalent to the classical density function. It is used to define a set of probabilities describing a statistical state of a system where all that is known is the probability of being in a given quantum state. The density operator must satisfy the equation of motion (Ref 78:380)

$$i\hbar \frac{d}{dt} \hat{\rho} = [\hat{H}, \hat{\rho}] \quad (B1)$$

where

\hat{H} = system Hamiltonian in the presence of an electromagnetic field

\hbar = planck's constant, \hbar , divided by 2π

i = complex imaginary; $\sqrt{-1}$

\hat{H}_0 = system Hamiltonian in the absence of the field.

$$\hat{\rho} = \sum_n P_n |n\rangle \langle n|$$

The difference between \hat{H}_0 and \hat{H} is due to the coupling of the system to the applied field. Following the standard quantum mechanical approach

$$\hat{H}_0 |n\rangle = E_n |n\rangle \quad (B2)$$

where $\langle \hat{H}_0 \rangle = E_n$, the allowed energy of the unperturbed system whose states are specified by the complete quantum descriptor n . The set

of eigenstates $\{n\}$ form a basis for a representation. Under the assumption that the system of molecules is in an initial equilibrium and is then perturbed by the presence of the applied field.

$$\hat{\rho}(t=0) = \hat{\rho}_0 \quad (B3)$$

Equation (B3) provides an initial condition to solve the equation of motion, Eq (B1). For a system initially in thermal equilibrium (Ref 48:40) the density operator may be written as

$$\hat{\rho}_0 = \frac{e^{-\hat{H}_0/kT}}{\sum_n e^{-E_n/kT}} \quad (B4)$$

and its matrix element is given by

$$\langle n | \hat{\rho}_0 | m \rangle = (\hat{\rho}_0)_{nm} = \frac{e^{-E_n/kT}}{\sum_n e^{-E_n/kT}} \delta_{nm} \quad (B5)$$

where

T = temperature

k = Boltzmann constant

δ_{nm} = Kronecker delta such that $\begin{cases} = 0, & n \neq m; \\ = 1, & n=m \end{cases}$

The density operator formalism can be used to determine the expectation value of any dynamic variable and therefore the physical character of a system at any time t .

The first step in this procedure is to determine the specific expression of the density operator for a system of particles in

$$i \hbar \frac{d}{dt} [\hat{\rho}_0 + \hat{\rho}_1(t) + \hat{\rho}_2(t) + \dots] = [\hat{H}_0, \hat{\rho}_0 + \hat{\rho}_1(t) + \hat{\rho}_2(t) + \dots] \\ + [\hat{H}_1(t), \hat{\rho}_0 + \hat{\rho}_1(t) + \hat{\rho}_2(t) + \dots] \quad (B10)$$

After equating terms involving the same powers of $\hat{H}_1(t)$ (e.g., $[\hat{H}_0, \hat{\rho}_0] \propto$ zero power, $[\hat{H}_0, \hat{\rho}_1(t)]$ and $[\hat{H}_1(t), \hat{\rho}_0] \propto [\hat{H}_1(t)]^1$, etc.), a set of equations is obtained

$$i \hbar \frac{d}{dt} \hat{\rho}_0 = [\hat{H}_0, \hat{\rho}_0] \\ i \hbar \frac{d}{dt} \hat{\rho}_1 = [\hat{H}_0, \hat{\rho}_1(t)] + [\hat{H}_1(t), \hat{\rho}_0] \\ i \hbar \frac{d}{dt} \hat{\rho}_2 = [\hat{H}_0, \hat{\rho}_2(t)] + [\hat{H}_1(t), \hat{\rho}_1(t)] \\ i \hbar \frac{d}{dt} \hat{\rho}_n = [\hat{H}_0, \hat{\rho}_n(t)] + [\hat{H}_1(t), \hat{\rho}_{n-1}(t)] \quad (B11)$$

Since $\hat{\rho}_0$, \hat{H}_0 and $\hat{H}_1(t)$ are known, the second equation in Eq (B11) can be solved for $\hat{\rho}_1(t)$ subject to the initial condition. This procedure can be repeated until the desired number of terms have been obtained in the series. The solution can be obtained using a method analogous to an integration factor (Ref 48:53) applied in general operator fashion as

$$V_0(t) \left\{ i \hbar \frac{d}{dt} \hat{\rho}_n(t) - [\hat{H}_0, \hat{\rho}_n(t)] \right\} U_0(t) = i \hbar \frac{d}{dt} \left\{ V_0(t) \hat{\rho}_n(t) U_0(t) \right\} \quad (B12)$$

where it is necessary to find the operators $V_0(t)$ and $U_0(t)$ that makes

this true. By expanding Eq (B12) it can be shown that the equality is true if the following two equations are satisfied

$$i\hbar \frac{d}{dt} V_0(t) = -V_0(t)\hat{H}_0$$

$$i\hbar \frac{d}{dt} U_0(t) = \hat{H}_0 U_0(t) \quad (B13)$$

The solutions to Eq (B13) are

$$V_0(t) = e^{i\hat{H}_0 t/\hbar}$$

$$U_0(t) = e^{-i\hat{H}_0 t/\hbar} \quad (B14)$$

so that $V_0(t) = U_0(-t)$ and the exponentials are defined by the power series. Since the various powers of \hat{H}_0 are commutable then $U_0(t)$, $U_0(t')$, $V_0(t)$ and $\hat{\rho}_0$ commute with each other. This property and those that follow will prove useful in the derivation of $\hat{\rho}_n(t)$.

- Properties:
- (i) $U_0(t)U_0(t') = U_0(t+t')$
 - (ii) $U_0(0) = 1$
 - (iii) $U_0(t)U_0(-t) = 1$
 - (iv) $U_0(t)V_0(t) = 1$ (B15)

properties (iii) and (iv) imply that $U_0(-t)$ and $V_0(t)$ are the inverse of $U_0(t)$. $U_0(t)$ is called the unperturbed time development operator. These operators transform from the Schrödinger picture into the interaction picture. The solution of the unperturbed time dependent Schrödinger equation

$$\hat{H}_0 \psi(t) = i\hbar \frac{d}{dt} \psi(t) \quad (B16)$$

can be obtained by

$$\psi(t) = U_0(t)\psi(0) = e^{-iH_0 t/\hbar} \psi(0) \quad (B17)$$

$U_0(t)$ and $V_0(t)$ can be used to obtain $\hat{\rho}_n(t)$ by multiplying the n terms in Eq (A11) by $U_0(t)$ on the right and $V_0(t) = U_0(-t)$ on the left. These factors are unique, except for a trivial multiplicative constant. This yields

$$i\hbar U_0(-t) \frac{d}{dt} \hat{\rho}_n U_0(t) = U_0(-t)[\hat{H}_0, \hat{\rho}_n(t)]U_0(t) + U_0(-t)[\hat{H}_1(t), \hat{\rho}_{n-1}(t)]U_0(t) \quad (B18)$$

Equation (B12) reduces this to

$$i\hbar \frac{d}{dt} \{ U_0(-t) \hat{\rho}_n(t) U_0(t) \} = U_0(-t)[\hat{H}_1(t), \hat{\rho}_{n-1}(t)]U_0(t) \quad (B19)$$

Integration from $-\infty$ to t yields

$$i\hbar U_0(-t) \hat{\rho}_n(t) U_0(t) = \int_{-\infty}^t dt_1 U_0(-t_1)[\hat{H}_1(t), \hat{\rho}_{n-1}(t_1)]U_0(t_1) \quad (B20)$$

where the lower limit is determined by the initial condition

$\hat{\rho}_n(-\infty) = 0$. Equation (B20) may be written more simply by defining

$$\hat{H}_1(t) = U_0(-t) \hat{H}_1(t) U_0(t) = e^{iH_0 t/\hbar} \hat{H}_1(t) e^{-iH_0 t/\hbar} \quad (B21)$$

which is in the interaction picture where time dependence is carried partly by both the operator and the state wave functions. This picture is intermediate to the Schrödinger picture where the operators don't depend on time but the wave functions do and the Heisenberg picture where the operators depend on time but the wave functions don't. Also, from the definition

$$\hat{\rho}_n(t) = U_0(-t)\hat{\rho}_n(t)U(t) \quad (B22)$$

Then upon substitution into Eq (B20) after it is expanded

$$\hat{\rho}_n(t) = (i\hbar)^{-1} \int_{-\infty}^t dt_1 [\hat{H}_1(t_1), U_0(-t)\hat{\rho}_{n-1}(t_1)U_0(t_1)] \quad (B23)$$

From this it is obvious that for $n=1$, $\hat{\rho}_1(t)$ can be expressed in terms of $\hat{\rho}_0(t)$.

$$\hat{\rho}_1(t) = (i\hbar)^{-1} \int_{-\infty}^t dt_1 [\hat{H}_1(t_1), U_0(-t)\hat{\rho}_0U_0(t)] \quad (B24)$$

Since ρ_0 and $U_0(-t)$ are both functions of \hat{H}_0 , they commute with each other so that

$$U_0(-t_1)\hat{\rho}_0 = \hat{\rho}_0U_0(-t_1)$$

and

$$U_0(-t_1)\hat{\rho}_0U_0(t) = \hat{\rho}_0$$

after the use of property (iii) in Eq (B15), $\hat{\rho}_0 = \hat{\rho}_0$. Then

$$\hat{\rho}_1(t) = (i\hbar)^{-1} \int_{-\infty}^t dt_1 [\hat{H}_1(t_1), \hat{\rho}_0] \quad (B25)$$

or

$$\hat{\rho}_1(t) = (i\hbar)^{-1} U_0(t) \left\{ \int_{-\infty}^t dt_1 [\hat{H}_1(t_1), \hat{\rho}_0] \right\} U_0(-t) \quad (B26)$$

to find $\hat{\rho}_2$ let $n=1$ in Eq (B23)

$$\hat{\rho}_2(t) = (i\hbar)^{-1} \int_{-\infty}^t dt_1 [\hat{H}_1(t_1), U_0(-t_1)\hat{\rho}_1(t_1)U_0(t)] \quad (B27)$$

which upon substituting for $\hat{\rho}_1(t_1)$ from Eq (B26) becomes

$$\hat{\rho}_2(t) = (i\hbar)^{-2} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 [\hat{H}_1(t_1), [\hat{H}_1(t_2), \hat{\rho}_0]] \quad (B28)$$

similarly

$$\hat{\rho}_3(t) = (i\hbar)^{-3} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 [\hat{H}_1(t_1), [\hat{H}_1(t_2), [\hat{H}_1(t_3), \hat{\rho}_0]]] \quad (B29)$$

or in general

$$\hat{\rho}_n(t) = (i\hbar)^{-n} \int_{-\infty}^t dt \int_{-\infty}^{t_1} dt \dots \int_{-\infty}^{t_{n-1}} dt_n [\hat{H}_1(t_1), [\hat{H}_1(t_2), [\dots [\hat{H}_1(t_n), \hat{\rho}_0] \dots]]] \quad (B30)$$

Then upon substitution of these expansion terms into Eq (B8), $\hat{\rho}(t)$ is known and may be used to determine the response of the system to external forces, both linear and nonlinear.

Appendix C: Molecular Polarizability

Just as on a macroscopic level the polarization \bar{P} is related to the electric field by the susceptibility tensor Eq (2.13), the induced dipole moment, \bar{d} , may be related to the electric field through the polarizability tensor, $\bar{\rho}$. The derivation of the molecular dipole moment is made here using the density operator results of Appendix B. From the definitions of $\langle \bar{d}^{(n)} \rangle$ given in Eq (3.8) and Eq (B30), each order of $\langle \bar{d} \rangle (t, \bar{r})$ for $n=1$ to 3 is obtained. From Eqs (B22) and (B25)

$$\langle \bar{d}^{(1)} \rangle = \text{Tr} \left\{ (i\hbar)^{-1} U_0(t) \int_{-\infty}^t dt_1 [\hat{H}_1(t_1), \hat{\rho}_0] U_0(-t_1) \bar{d}(t_1, \bar{r}) \right\} \quad (C1)$$

For

$$\hat{H}_1(t) = - \bar{d}(\bar{r}, t) \cdot \bar{E}(\bar{r}, t) \quad (C2)$$

substituted into Eq (B21)

$$\hat{H}_1(t) = e^{i\hat{H}_0 t/\hbar} [-\bar{d}(t, \bar{r}) \cdot \bar{E}(t)] e^{-i\hat{H}_0 t/\hbar} \quad (C3)$$

Note that \bar{E} , being a nonoperator, commutes with all operators, so that one gets

$$\hat{H}_1(t) = -e^{i\hat{H}_0 t/\hbar} \bar{d}(t, \bar{r}) e^{-i\hat{H}_0 t/\hbar} \cdot \bar{E}(t) \quad (C4)$$

or

$$\hat{H}_1(t) = -e^{i\hat{H}_0 t/\hbar} d_\alpha(t, \bar{r}) e^{-i\hat{H}_0 t/\hbar} E_\alpha(t) \quad (C5)$$

Recalling that $\bar{d}(r) = \sum_{i=1}^m q_i \bar{r}_i$ is the dipole moment in the Schrödinger picture, the time dependent dipole moment in the

interaction picture is defined as

$$\bar{d}(t, r) = e^{i\hat{H}_0 t/\hbar} \bar{d}(r) e^{-i\hat{H}_0 t/\hbar} = U_0(-t) \bar{d}(r) U_0(t) \quad (C6)$$

then

$$\hat{H}_1(t) = - \hat{d}_\alpha(t) E_\alpha(t) \quad (C7)$$

where the spatial dependence of d has been suppressed for convenience.

When Eq (C7), the commutation term is used, Eq (C1) may be written as

$$[\hat{H}_1(t), \hat{\rho}_0] = - [\hat{d}_\alpha(t) E_\alpha(t) \hat{\rho}_0 - \hat{\rho}_0 \hat{d}_\alpha(t) E_\alpha(t)] \quad (C8)$$

Since $E_\alpha(t)$ is a scalar function, it commutes with all operators and may be factored to yield

$$[\hat{H}_1(t), \hat{\rho}_0] = - [\hat{d}_\alpha(t) \hat{\rho}_0 - \hat{\rho}_0 \hat{d}_\alpha(t)] E_\alpha(t) \quad (C9)$$

$$[\hat{H}_1(t), \hat{\rho}_0] = - [\hat{d}_\alpha(t), \hat{\rho}_0] E_\alpha(t) \quad (C10)$$

Equation (C1) after using Eq (C10) becomes

$$\langle d_\mu^{(1)} \rangle = - \text{Tr} \left\{ (i\hbar)^{-1} U_0(t) \int_{-\infty}^t dt_1 [\hat{d}_\alpha(t_1), \hat{\rho}_0] E_\alpha(t_1) U_0(-t) \hat{d}_\mu \right\} \quad (C11)$$

From the linearity of the trace, the integration may be performed after taking the trace. Since $U_0(t)$ and $U_0(-t)$ are not functions of the variable t_1 Eq (C11) becomes

$$\langle d_\mu^{(1)} \rangle = - (i\hbar)^{-1} \int_{-\infty}^t dt_1 E_\alpha(t_1) \text{Tr} \left\{ U_0(t) [\hat{d}_\alpha(t_1), \hat{\rho}_0] U_0(-t) \hat{d}_\mu \right\} \quad (C12)$$

From the Fourier transform of $E_\alpha(t)$ given by Eq (A22) and by noting that

$$e^{-i\omega t_1} = e^{-i\omega t_1} e^{i\omega t} \quad e^{-i\omega t} = e^{-i\omega t} e^{-i\omega(t_1-t)}$$

Eq (C12) is

$$\langle d_{\mu}^{(1)} \rangle = - (i\hbar)^{-1} \int_{-\infty}^t dt_1 \int_{-\infty}^{\infty} d\omega E_{\alpha}(\omega) e^{i\omega t} e^{-i\omega(t_1-t)} \text{Tr} \left\{ U_0(t) [\hat{d}_{\alpha}(t_1), \hat{\rho}_0] \right. \\ \left. \times U_0(-t) \hat{d}_{\mu} \right\} \quad (C13)$$

This can be rewritten as

$$\langle d_{\mu}^{(1)} \rangle = - \int_{-\infty}^{\infty} d\omega \left\{ (i\hbar)^{-1} \int_{-\infty}^t dt_1 \text{Tr} \left\{ U_0(t) [\hat{d}_{\alpha}(t_1), \hat{\rho}_0] U_0(-t) \hat{d}_{\mu} \right\} e^{-i\omega(t_1-t)} \right. \\ \left. \times E_{\alpha}(\omega) e^{-i\omega t} \right\} \quad (C14)$$

The polarizability tensor of the first order, $p_{\mu\alpha}^{(1)}$, is defined as

$$p_{\mu\alpha}^{(1)}(\omega) = - (i\hbar)^{-1} \int_{-\infty}^t dt_1 \text{Tr} \left\{ U_0(t) [\hat{d}_{\alpha}(t_1), \hat{\rho}_0] U_0(-t) \hat{d}_{\mu} \right\} e^{-i\omega(t_1-t)} \quad (C15)$$

It will be made clear that $p_{\mu\alpha}^{(1)}$ is a function of ω by eliminating the t from this expression in a straightforward manner.

$$U_0(t) [\hat{d}_{\alpha}(t_1), \hat{\rho}_0] U_0(-t) \\ = U_0(t) [\hat{d}_{\alpha}(t_1) U_0(-t) U_0(t) \hat{\rho}_0 - \hat{\rho}_0 U_0(-t) U_0(t) \hat{d}_{\alpha}(t_1)] U_0(-t) \quad (C16)$$

$$= U_0(t) \hat{d}_{\alpha}(t) U_0(-t) U_0(t) \hat{\rho}_0 U_0(-t) - U_0(t) \hat{\rho}_0 U_0(-t) U_0(t) \hat{d}_{\alpha}(t_1) U_0(-t) \\ \quad (C17)$$

where $U_0(-t) U_0(t) = 1$ has been used. From the definition of $\hat{d}_{\alpha}(t)$ in Eq (C6), U in Eq (B15) and the commutation property of $\hat{\rho}_0 U_0(-t)$ and $U_0(t) \hat{\rho}_0$, Eq (C17) becomes

$$= U_0(t_1-t) \hat{d}_\alpha U_0(t-t_1) \hat{\rho}_0 - \hat{\rho}_0 U_0(t_1-t) \hat{d}_\alpha U_0(t-t_1) \quad (C18)$$

or

$$= \hat{d}_\alpha(t-t_1) \hat{\rho}_0 - \hat{\rho}_0 \hat{d}_\alpha(t-t_1) = [\hat{d}_\alpha(t-t_1), \hat{\rho}_0] \quad (C19)$$

Then

$$p_{\mu\alpha}^{(1)} = -(i\hbar)^{-1} \int_{-\infty}^t dt_1 \text{Tr} \left\{ [\hat{d}_\alpha(t_1-t), \hat{\rho}_0] \hat{d}_\mu \right\} e^{-i\omega(t_1-t)} \quad (C20)$$

With the change of variables

$$\tau = t_1 - t ; \quad d\tau = dt_1$$

and limits

$$t_1 = t \rightarrow \tau = 0$$

$$t_1 = -\infty \rightarrow \tau = -\infty$$

first, then the change $t_1 = \tau$

$$p_{\mu\alpha}^{(1)} = -(i\hbar)^{-1} \int_{-\infty}^0 dt_1 \text{Tr} \left\{ [\hat{d}_\alpha(t_1), \hat{\rho}_0] \hat{d}_\mu \right\} e^{-i\omega t_1} \quad (C21)$$

The trace is

$$\text{Tr} [\hat{d}_\alpha(t_1), \hat{\rho}_0] \hat{d}_\mu = \text{Tr} \left\{ \hat{d}_\alpha(t_1) \hat{\rho}_0 \hat{d}_\mu - \hat{\rho}_0 \hat{d}_\alpha(t_1) \hat{d}_\mu \right\} \quad (C22)$$

A property of the trace is its invariance under cyclic permutation of the arguments. Equation (C22) is therefore

$$\begin{aligned}
&= \text{Tr} \left\{ \hat{\rho}_0 \hat{d}_\mu \hat{d}_\alpha(t_1) - \hat{\rho}_0 \hat{d}_\alpha(t_1) \hat{d}_\mu \right\} \\
&= \text{Tr} \hat{\rho}_0 [\hat{d}_\mu, \hat{d}_\alpha(t_1)]
\end{aligned} \tag{C23}$$

The first order polarizability tensor is then

$$p_{\mu\alpha}^{(1)}(\omega) = -(i\hbar)^{-1} \int_{-\infty}^0 dt_1 \text{Tr} \left\{ \hat{\rho}_0 [\hat{d}_\mu, \hat{d}_\alpha(t_1)] \right\} e^{i\omega t_1} \tag{C24}$$

which is the desired result for the first order term.

For completeness, expressions for $p_{\mu\alpha\beta}^{(2)}$ and $p_{\mu\alpha\beta\gamma}^{(3)}$ are obtained before writing down the generalized n^{th} order term. From Eq (3.7) and Eq (B28) the expectation value is

$$\langle d_\mu^{(2)} \rangle = \text{Tr} \left\{ (i\hbar)^{-2} U_0(t) \int_{-\infty}^t dt_1 \int_{-\infty}^t dt_2 [\hat{H}_1(t_1), [\hat{H}_1(t_2), \hat{\rho}_0]] U_0(-t) \hat{d}_\mu \right\} \tag{C25}$$

where with the dipole approximation to the perturbation energy is given by Eq (C7)

$$[\hat{H}_1(t_2), \hat{\rho}_0] = -E_\beta(t_2) [\hat{d}_\beta(t_2), \hat{\rho}_0] \tag{C26}$$

In a similar procedure to that used for Eq (C10)

$$\begin{aligned}
[\hat{H}_1(t_1), [\hat{H}_1(t_2), \hat{\rho}_0]] &= [-\hat{d}_\alpha(t_1) E_\alpha(t_1), -E_\beta(t_2) [\hat{d}_\beta(t_2), \hat{\rho}_0]] \\
&= E_\alpha(t_1) E_\beta(t_2) [\hat{d}_\alpha(t_1), [\hat{d}_\beta(t_2), \hat{\rho}_0]]
\end{aligned} \tag{C27}$$

Upon use of the Fourier transform definition of $E_\alpha(t_1)$ and $E_\beta(t_2)$, $\langle d_\mu^{(2)} \rangle$ becomes

$$\langle d_{\mu}^{(2)} \rangle = (i\hbar)^{-2} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{\infty} d\omega_1 E_{\alpha}(\omega_1) e^{-i\omega_1 t_1} e^{-i\omega_1(t_1-t)} \int_{-\infty}^{\infty} d\omega_2 E_{\beta}(\omega_2) e^{-i\omega_2 t} \\ \times e^{-i\omega_2(t_2-t)} \text{Tr} \left\{ U_0(t) [\hat{d}_{\alpha}(t_1), [\hat{d}_{\beta}(t_2), \hat{\rho}_0]] U_0(-t) \hat{d}_{\mu} \right\} \quad (C28)$$

$p_{\mu\alpha\beta}^{(2)}$ is defined as

$$p_{\mu\alpha\beta}^{(2)} = (i\hbar)^{-2} \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \text{Tr} \left\{ U_0(t) [\hat{d}_{\alpha}(t_1), [\hat{d}_{\beta}(t_2), \hat{\rho}_0]] U_0(-t) \hat{d}_{\mu} \right\} \\ \times e^{-i\omega_1(t_1-t)} e^{-i\omega_2(t_2-t)} \quad (C29)$$

To eliminate t from this expression, use the results of Eqs (C18) and (C19) for t_1 and a similar set for t_2 with the result

$$U_0(t) [\hat{d}_{\alpha}(t_1), [\hat{d}_{\beta}(t_2), \hat{\rho}_0]] U_0(-t) = [\hat{d}_{\alpha}(t_1-t), [\hat{d}_{\beta}(t_2-t), \hat{\rho}_0]] \quad (C30)$$

Let $t_2-t \rightarrow t_2$ $dt_2 \rightarrow dt_2$

$t_1-t \rightarrow t_1$ $dt_1 \rightarrow dt_1$

With the proper change of limits on both integrals of Eq (C29), it becomes

$$p_{\mu\alpha\beta}^{(2)} (\omega_1, \omega_2) = (i\hbar)^{-2} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \text{Tr} \left\{ [\hat{d}_{\alpha}(t_1), [\hat{d}_{\beta}(t_2), \hat{\rho}_0]] \hat{d}_{\mu} \right\} e^{-\omega_1 t_1} e^{-i\omega_2 t_2} \quad (C31)$$

By using the trace cyclic permutation property after expansion, the trace in Eq (C31) becomes

$$\begin{aligned}
& \text{Tr} \left\{ \hat{d}_\alpha(t_1) \hat{d}_\beta(t_2) \hat{\rho}_0 \hat{d}_\mu - \hat{d}_\beta(t_2) \hat{\rho}_0 \hat{d}_\alpha(t_1) \hat{d}_\mu - \hat{d}_\alpha(t_1) \hat{\rho}_0 \hat{d}_\beta(t_2) \hat{d}_\mu + \hat{\rho}_0 \hat{d}_\beta(t_2) \hat{d}_\alpha(t_1) \hat{d}_\mu \right\} \\
&= \text{Tr} \left\{ \hat{\rho}_0 \hat{d}_\mu \hat{d}_\alpha(t_1) \hat{d}_\beta(t_2) - \hat{\rho}_0 \hat{d}_\alpha(t_1) \hat{d}_\mu \hat{d}_\beta(t_2) \right. \\
&\quad \left. - \hat{\rho}_0 \hat{d}_\beta(t_2) \hat{d}_\mu \hat{d}_\alpha(t_1) + \hat{\rho}_0 \hat{d}_\beta(t_2) \hat{d}_\alpha(t_1) \hat{d}_\mu \right\} \\
&= \text{Tr} \left\{ \hat{\rho}_0 [[\hat{d}_\mu, \hat{d}_\alpha(t_1)], \hat{d}_\beta(t_2)] \right\}
\end{aligned}$$

The second order polarizability tensor is then

$$\begin{aligned}
p_{\mu\alpha\beta}^{(2)}(\omega_1, \omega_2) &= (i\hbar)^{-2} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \text{Tr} \left\{ \hat{\rho}_0 [[\hat{d}_\mu, \hat{d}_\alpha(t_1)], \hat{d}_\beta(t_2)] \right\} \\
&\quad \times e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} \quad (C32)
\end{aligned}$$

While this expression for $p_{\mu\alpha\beta}^{(3)}$ is valid, it does not have the intrinsic permutation symmetry specified for $x_{\mu\alpha\beta}^{(2)}(\omega_1, \omega_2)$. Therefore, if $p_{\mu\alpha\beta}^{(2)}(\omega_1, \omega_2)$ is to form the basis for $x_{\mu\alpha\beta}^{(2)}$ then this symmetry must be accounted for in the equation. Since there was no particular requirement to select α, β and ω_1, ω_2 in the order used, the result is perfectly valid if written

$$\begin{aligned}
p_{\mu\beta\alpha}^{(2)}(\omega_2, \omega_1) &= (i\hbar)^{-2} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \text{Tr} \left\{ \hat{\rho}_0 [[\hat{d}_\mu, \hat{d}_\beta(t_1)], \hat{d}_\alpha(t_2)] \right\} \\
&\quad \times e^{-i\omega_2 t_1} e^{-i\omega_1 t_2} \quad (C33)
\end{aligned}$$

Upon adding this result to that of $p_{\mu\alpha\beta}^{(2)}$ in Eq (C32), a quantity having the desired symmetry results

$$p_{\mu\alpha\beta}^{(2)}(\omega_1, \omega_2) + p_{\mu\beta\alpha}^{(2)}(\omega_2, \omega_1) \quad (C34)$$

In order to retain the same magnitude for the case where $\alpha = \beta$ and $\omega_1 = \omega_2$, a factor of 1/2 can be used. With these changes

$$p_{\mu\alpha\beta}^{(2)}(\omega_1, \omega_2) = 1/2 (i\hbar)^{-2} S_{(\alpha, \omega)} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \text{Tr}\left\{\rho_0[[d_\mu, d_\alpha(t_1)], d_\beta(t_2)]\right\} e^{-i\omega_1 t_1} e^{-i\omega_2 t_2} \quad (C35)$$

Where $S_{(\alpha, \omega)}$ is the symmetrizing operator defined such that the term(s) operated upon is to be summed over all of the possible permutations of the pairs (α, ω_1) and (β, ω_2) .

For the third order polarizability tensor, $p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}$ Eq (B29) is used for $\langle d_\mu^{(3)} \rangle$ with the result

$$\begin{aligned} \langle d_\mu^{(3)} \rangle &= \text{Tr}\left\{(-i\hbar)^{-3} U_0(t) \int_{-\infty}^t dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \right. \\ &\quad \times \left. [\hat{H}'(t_1), [\hat{H}'(t_2), [\hat{H}'(t_3), \hat{\rho}_0]]] U_0(-t) \hat{d}_\mu \right\} \quad (C36) \end{aligned}$$

Again Eq (C7) is used for the electric dipole approximation to the perturbation energy yielding the result

$$[\hat{H}'(t_3), \hat{\rho}_0] = -E_{\alpha_3}(t_3) [\hat{d}_{\alpha_3}(t_3), \hat{\rho}_0] \quad (i)$$

$$[\hat{H}'(t_2), [\hat{H}'(t_3), \hat{\rho}_0]] = E_{\alpha_2}(t_2) E_{\alpha_3}(t_3) [\hat{d}_{\alpha_2}(t_2), [\hat{d}_{\alpha_3}(t_3), \hat{\rho}_0]] \quad (ii)$$

$$[\hat{H}'(t_1), [\hat{H}'(t_2), [\hat{H}'(t_3), \hat{\rho}_0]]] = -E_{\alpha_1}(t_1) E_{\alpha_2}(t_2) E_{\alpha_3}(t_3) \quad (iii)$$

$$[\hat{d}_{\alpha_1}(t_1), [\hat{d}_{\alpha_2}(t_2), [\hat{d}_{\alpha_3}(t_3), \hat{\rho}_0]]] \quad (C37)$$

where the commutation property of a scalar has again been used. Upon substitution of this result into Eq (C36) for $\langle d_\mu^{(3)} \rangle$, removal of the scalar terms $E_{\alpha_i}(t_i)$ from the trace and use of the Fourier transform of $E_{\alpha_i}(t_i)$, the dipole moment value is

$$\begin{aligned}
\langle d_{\mu}^{(3)} \rangle &= (-i\hbar)^{-3} \int_{-\infty}^{\infty} d\omega_1 \int_{-\infty}^{\infty} d\omega_2 \int_{-\infty}^{\infty} d\omega_3 \left(\int_{-\infty}^t dt_1 \quad \int_{-\infty}^{t_1} dt_2 \quad \int_{-\infty}^{t_2} dt_3 \right. \\
&\times \left. \text{Tr} \left\{ U_0(t) [\hat{d}_{\alpha_1}(t_1), [\hat{d}_{\alpha_2}(t_2), \right. \right. \\
&\times \left. \left. [\hat{d}_{\alpha_3}(t_3), \hat{\rho}_0]] \right] U_0(-t) \hat{d}_{\mu} \right\} e^{-i[\omega_1(t_1-t) + \omega_2(t_2-t) + \omega_3(t_3-t)]} \\
&\times E_{\alpha_1}(\omega_1) E_{\alpha_2}(\omega_2) E_{\alpha_3}(\omega_3) e^{-i(\omega_1+\omega_2+\omega_3)t} \quad (C38)
\end{aligned}$$

t can be eliminated from the terms in brackets on the right hand side by an extension of the expression in Eq (C19)

$$\begin{aligned}
U_0(t) [\hat{d}_{\alpha_1}(t_1), [\hat{d}_{\alpha_2}(t_2), [\hat{d}_{\alpha_3}(t_3), \hat{\rho}_0]]] U_0(-t) &= [\hat{d}_{\alpha_1}(t_1-t), [\hat{d}_{\alpha_2}(t_2-t), \\
&[\hat{d}_{\alpha_3}(t_3-t), \hat{\rho}_0]]] \quad (C39)
\end{aligned}$$

With the simultaneous change of variables

$$\begin{aligned}
t_3 - t &\rightarrow t_3 \\
t_2 - t &\rightarrow t_2 \\
t_1 - t &\rightarrow t_1
\end{aligned}$$

and the proper change to the limits of integration, the definition of $p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}$ is

$$\begin{aligned}
p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) &= (-i\hbar)^{-3} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \text{Tr} \left\{ [\hat{d}_{\alpha_1}(t_1), [\hat{d}_{\alpha_2}(t_2), [\hat{d}_{\alpha_3}(t_3), \right. \\
&\left. \hat{\rho}_0]]] \hat{d}_{\mu} \right\} e^{-i[\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3]} \quad (C40)
\end{aligned}$$

The use of the cyclic permutation property of the trace gives the change

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) = (-i\hbar)^{-3} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3$$

$$\times \text{Tr} \left\{ \hat{\rho}_0 [[[\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)], \hat{d}_{\alpha_2}(t_2)], \hat{d}_{\alpha_3}(t_3)] \right\} e^{-i[\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3]} \quad (\text{C41})$$

To insure that intrinsic permutation symmetry holds

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)} \rightarrow \frac{1}{6} (p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) + p_{\mu\alpha_2\alpha_1\alpha_3}^{(3)}(\omega_2, \omega_1, \omega_3) + p_{\mu\alpha_2\alpha_3\alpha_1}^{(3)}(\omega_2, \omega_3, \omega_1)$$

$$+ p_{\mu\alpha_1\alpha_3\alpha_2}^{(3)}(\omega_1, \omega_3, \omega_2) + p_{\mu\alpha_3\alpha_2\alpha_1}^{(3)}(\omega_3, \omega_2, \omega_1) + p_{\mu\alpha_3\alpha_1\alpha_2}^{(3)}(\omega_3, \omega_1, \omega_2))$$

$$= \frac{1}{3!} \sum_{(\alpha, \omega)} p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) \quad (\text{C42})$$

The factor 1/6 insures that the magnitude will remain the same. This sum relies on the fact that the subscript and frequency indices were arbitrarily chosen. Thus

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{1}{3!} \sum_{(\alpha, \omega)} (-i\hbar)^{-3} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3$$

$$\times \text{Tr} \left\{ \hat{\rho}_0 [[[\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)], \hat{d}_{\alpha_2}(t_2)], \hat{d}_{\alpha_3}(t_3)] \right\} e^{-i[\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3]} \quad (\text{C43})$$

A generalization of this can then be made to the polarizability order n (Ref 48:65)

$$p_{\mu\alpha \dots \alpha_n}^{(n)}(\omega_1, \dots, \omega_n) = \frac{1}{n!} \sum_{(\alpha, \omega)} (-i\hbar)^{-n} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \dots$$

$$\int_{-\infty}^{t_{n-1}} dt_n \text{Tr} \left\{ \hat{\rho}_0 [\dots [[\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)], \hat{d}_{\alpha_2}(t_2)], \dots], \hat{d}_{\alpha_n}(t_n)] \right\} e^{-i \sum_{m=1}^n \omega_m t_m} \quad (\text{C44})$$

The assumptions made in obtaining these results are:

- (1) The contribution of the magnetic field of the light beams is neglected as small compared to that of the electric dipole moment.
- (2) The intrinsic permutation symmetry for the susceptibility arising from the form of the polarization expression is required to carry over to the various orders of the polarizability.
- (3) The energy added to the system by the interaction of the field with the dipole moment is of a small enough magnitude that the perturbation approach applies.
- (4) Causality and reality conditions apply.
- (5) The expression for $\hat{\rho}_0$ results from the molecular system being in equilibrium.
- (6) The perturbing force is zero at some time in the past so that $\hat{\rho}_n(-\infty) = \hat{\rho}_0$.

In addition to these assumptions it should be noted that

$\hat{d}_\mu(\tau) = U_0(-\tau)\hat{d}_\mu U_0(\tau)$ and that \hat{d}_μ is not a function of time but represents the time independent dipole moment operator of the molecular system in the Schrödinger picture.

The results obtained in this appendix are valid within the assumptions made whether the dipole moments are similarly or randomly oriented. For a similar orientation, orientational averaging results

only in multiplying by the number of moments in the volume of interest. In this case, $N_p(n)$ _{μ} would represent the susceptibility $x(n)$ _{μ} directly.

Appendix D: Electric Field Functions

The third order polarizability has been derived in Appendix C as a function of frequency. The electric field, however, is normally specified as a function of time. For use with the polarizability, the electric field as a function of frequency, is obtained in this appendix.

A real electric field $E'(t)$ may be expressed as

$$E'(t) = f(t) + f^*(t) \quad (D1)$$

The Fourier transform to frequency space is

$$E(\omega) = F[E'(t)] = F[f(t)] + F[f^*(t)] \quad (D2)$$

where $F[]$ represents the Fourier transform so that

$$F[f(t)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau f(\tau) e^{i\omega\tau} = \epsilon(\omega) \quad (D3)$$

$$F[f^*(t)] = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau f^*(\tau) e^{i\omega\tau} \quad (D4)$$

From Eq (D3) and with ω allowed to be complex, the transform of $f(t)$ can be written as

$$\epsilon(-\omega^*) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau f(\tau) e^{i(-\omega^*)\tau} \quad (D5)$$

$$[\epsilon(-\omega^*)]^* = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau f^*(\tau) e^{i\omega\tau} \quad (D6)$$

Thus, Eq (D6) equals Eq (D4)

$$[\epsilon(-\omega^*)]^* = F[f^*(t)] \quad (D7)$$

then

$$E(\omega) = \varepsilon(\omega) + [\varepsilon(-\omega^*)]^* \quad (D8)$$

or

$$E(\omega) = \varepsilon(\omega) + \varepsilon^*(-\omega) \quad (D9)$$

It is easily shown that $E(\omega)$ meets the reality condition

$E(-\omega^*) = [E(\omega)]^*$. From Eq (D9)

$$[E(\omega)]^* = \varepsilon^*(\omega^*) + \varepsilon(-\omega^*) \quad (D10)$$

and

$$E(-\omega^*) = \varepsilon(-\omega^*) + \varepsilon^*(\omega^*) \quad (D11)$$

thus Eqs (D10) and (D11) are equal and

$$E(-\omega^*) = [E(\omega)]^* \quad (D12)$$

It is also obvious that $[\varepsilon(\omega)]^* \neq \varepsilon(-\omega^*)$ unless $f(t)$ is a real function.

Appendix E: Molecular Polarizability Equation

The specific form of the third order polarizability Eq can be obtained using the general results of Appendix C, Eq (C43)

$$p_{\mu\alpha\alpha}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{1}{3!} \sum_{(\alpha, \omega)} (-i\hbar)^{-3} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \\ \text{Tr} \left\{ \hat{\rho}_0 [[[\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)], \hat{d}_{\alpha_2}(t_2)], \hat{d}_{\alpha_3}(t_3)] \right\} e^{-i[\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3]} \quad (\text{E1})$$

For the individual molecule in thermal equilibrium, Eq (B4) gives the density operator as

$$\hat{\rho}_0 = \frac{e^{-\hat{H}_0/kT}}{\sum_n e^{-E_n/kT}} \quad (\text{E2})$$

with

$$\zeta = (\sum_n e^{-E_n/kT})^{-1} \quad (\text{E3})$$

Eq (E2) can be written as

$$\hat{\rho}_0 = \zeta e^{-\hat{H}_0/kT} \quad (\text{E4})$$

This is used in Eq (E1) to obtain the third order polarizability, but first, expand the term inside of the trace in Eq (E1)

$$[\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)] = (\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)) - \hat{d}_{\alpha_1}(t_1)\hat{d}_\mu \\ [[\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)], \hat{d}_{\alpha_2}(t_2)] = \hat{d}_\mu \hat{d}_{\alpha_1}(t_1) \hat{d}_{\alpha_2}(t_2) - \hat{d}_{\alpha_2}(t_2) \hat{d}_\mu \hat{d}_{\alpha_1} \\ - \hat{d}_{\alpha_1}(t_1) \hat{d}_\mu \hat{d}_{\alpha_2}(t_2) + \hat{d}_{\alpha_2}(t_2) \hat{d}_{\alpha_1}(t_1) \hat{d}_\mu \quad (\text{E5})$$

$$\begin{aligned}
& [[[\hat{d}_\mu, \hat{d}_{\alpha_1}(t_1)], \hat{d}_{\alpha_2}(t_2)], \hat{d}_{\alpha_3}(t_3)] = \\
& \quad \hat{d}_\mu \hat{d}_{\alpha_1}(t_1) \hat{d}_{\alpha_2}(t_2) \hat{d}_{\alpha_3}(t_3) - \hat{d}_{\alpha_3}(t_3) \hat{d}_\mu \hat{d}_{\alpha_1}(t_1) \hat{d}_{\alpha_2}(t_2) \\
& \quad - \hat{d}_{\alpha_2}(t_2) \hat{d}_\mu \hat{d}_{\alpha_1}(t_1) \hat{d}_{\alpha_3}(t_3) + \hat{d}_{\alpha_3}(t_3) \hat{d}_{\alpha_2}(t_2) \hat{d}_\mu \hat{d}_{\alpha_1}(t_1) \\
& \quad - \hat{d}_{\alpha_1}(t_1) \hat{d}_\mu \hat{d}_{\alpha_2}(t_2) \hat{d}_{\alpha_3}(t_3) + \hat{d}_{\alpha_3}(t_3) \hat{d}_{\alpha_1}(t_1) \hat{d}_\mu \hat{d}_{\alpha_2}(t_2) \\
& \quad + \hat{d}_{\alpha_2}(t_2) \hat{d}_{\alpha_1}(t_1) \hat{d}_\mu \hat{d}_{\alpha_3}(t_3) - \hat{d}_{\alpha_3}(t_3) \hat{d}_{\alpha_2}(t_2) \hat{d}_{\alpha_1}(t_1) \hat{d}_\mu
\end{aligned} \tag{E6}$$

Note that the trace of an operator is defined by

$$\text{Tr}\{\hat{A}\} = \sum_a A_{aa} = \sum_a \langle a | \hat{A} | a \rangle \tag{E7}$$

where the states "a" are a complete basis for a representation. Thus in the energy representation,

$$\begin{aligned}
[\hat{\rho}_0]_{ab} &= \langle a | \hat{\rho}_0 | b \rangle = \langle a | \zeta e^{-\hat{H}_0/kT} | b \rangle \\
[\hat{\rho}_0]_{ab} &= \zeta e^{-E_a/kT} \langle a | b \rangle = \zeta e^{-E_a/kT} \delta_{ab}
\end{aligned} \tag{E8}$$

and

$$[\hat{\rho}_0]_{aa} = \zeta e^{-E_a/kT} = \rho_0^a \tag{E9}$$

Also, the definition of $d_\alpha(t)$, Eq (C6), is

$$\hat{d}_\alpha(t) = U_0(-t) \hat{d}_\alpha U_0(t) \tag{E10}$$

With the definition of $U(t)$ from Eq (B14)

$$U(t) = e^{-i\hat{H}_0 t/\hbar} \tag{E11}$$

The basis to evaluate the trace is available. Then, the dipole matrix element is

$$\begin{aligned}
 [\hat{d}_\alpha(t)]_{ab} &= \langle a | \hat{d}_\alpha(t) | b \rangle = \langle a | e^{i\hat{H}_0 t/\hbar} \hat{d}_\alpha e^{-i\hat{H}_0 t/\hbar} | b \rangle \\
 [\hat{d}_\alpha(t)]_{ab} &= e^{iE_a t/\hbar} \langle a | \hat{d}_\alpha | b \rangle e^{-iE_b t/\hbar} \\
 [\hat{d}_\alpha(t)]_{ab} &= e^{i\omega_{ab} t} d_{ab}^\alpha
 \end{aligned} \tag{E12}$$

where

$$\omega_{ab} = (E_a - E_b)/\hbar \tag{E13}$$

$$d_{ab}^\alpha = \langle a | \hat{d}_\alpha | b \rangle \tag{E14}$$

With the linear property of the trace these relations can be applied to the first term in Eq (E6). This serves to show how each of the terms can be developed.

$$\begin{aligned}
 \text{Tr}\left\{\hat{\rho}_0 \hat{d}_\mu \hat{d}_{\alpha_1}(t_1) \hat{d}_{\alpha_2}(t_2) \hat{d}_{\alpha_3}(t_3)\right\} &= \\
 \sum_a \langle a | \hat{\rho}_0 \hat{d}_\mu \hat{d}_{\alpha_1}(t_1) \hat{d}_{\alpha_2}(t_2) \hat{d}_{\alpha_3}(t_3) | a \rangle \\
 \text{Tr}\left\{\right\} &= \sum_a e^{-E_a/kT} \langle a | d_\mu d_{\alpha_1}(t_1) d_{\alpha_2}(t_2) d_{\alpha_3}(t_3) | a \rangle \\
 \text{Tr}\left\{\right\} &= \sum_a \rho_{aa}^o \sum_{b,c,d} \langle a | \hat{d}_\mu | b \rangle \langle b | \hat{d}_{\alpha_1}(t_1) | c \rangle \\
 &\quad \times \langle c | \hat{d}_{\alpha_2}(t_2) | d \rangle \langle d | \hat{d}_{\alpha_3}(t_3) | a \rangle
 \end{aligned} \tag{E15}$$

where the closure property, $\sum_i | i \rangle \langle i | = 1$, has been used. Upon use of Eq (E12)

$$\text{Tr} \left\{ \right\} = \sum_{\substack{a,b \\ c,d}} \rho_{aa}^o d_{ab}^\mu e^{i\omega_{bc}t_1} d_{bc}^{\alpha_1} e^{i\omega_{cd}t_2} d_{cd}^{\alpha_2} e^{i\omega_{da}t_3} d_{da}^{\alpha_3}$$

$$\text{Tr} \left\{ \right\} = \sum_{\substack{a,b \\ c,d}} \rho_{aa}^o d_{ab}^\mu d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3} e^{i(\omega_{bc}t_1 + \omega_{cd}t_2 + \omega_{da}t_3)} \quad (\text{E16})$$

When this term is placed in the integral of Eq (E1), the result is

$$\begin{aligned} & \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \text{Tr} \left\{ \right\} e^{-i(\omega_1 t_1 + \omega_2 t_2 + \omega_3 t_3)} \\ &= \sum_{\substack{a,b,c,d}} \int_{-\infty}^0 dt_1 \int_{-\infty}^{t_1} dt_2 \int_{-\infty}^{t_2} dt_3 \rho_{aa}^o d_{ab}^\mu d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3} \\ & \quad \times e^{i(\omega_{bc} - \omega_1)t_1} e^{i(\omega_{cd} - \omega_2)t_2} e^{i(\omega_{da} - \omega_3)t_3} \quad (\text{E17}) \end{aligned}$$

The integration over t_3 , t_2 , and t_1 can be performed to yield the following terms, respectively

wrt t_3

$$\frac{1}{i} \sum_{a,b,c,d} \rho_{aa}^o \frac{d_{ab}^\mu d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{da} - \omega_3)} e^{i(\omega_{bc} - \omega_1)t_1} e^{i(\omega_{cd} - \omega_2 + \omega_{da} - \omega_3)t_2}$$

wrt t_2

$$\frac{1}{i^2} \sum_{a,b,c,d} \rho_{aa}^o \frac{d_{ab}^\mu d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{da} - \omega_3)(\omega_{ca} - \omega_2 - \omega_3)} e^{i(\omega_{bc} - \omega_1 + \omega_{ca} - \omega_2 - \omega_3)t_1}$$

wrt t_1

$$\frac{1}{i^3} \sum_{a,b,c,d} \rho_{aa}^o \frac{d_{ab}^\mu d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{da} - \omega_3)(\omega_{ca} - \omega_2 - \omega_3)(\omega_{ba} - \omega_1 - \omega_2 - \omega_3)}$$

where the definition of ω_{ij} from Eq (E13) has been used. After these steps have been carried out for each of the terms in Eq (E6), the result is

$$\begin{aligned}
 p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) = & \frac{1}{3!} \sum_{(\alpha\omega)} (-i^2\hbar)^3 \sum_{a,b,c,d} \rho_{aa}^{\circ} \\
 & \left[\frac{d_{ab}^{\mu} d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{ba}-\omega_1-\omega_2-\omega_3)(\omega_{ca}-\omega_2-\omega_3)(\omega_{da}-\omega_3)} - \frac{d_{ab}^{\alpha_3} d_{bc}^{\mu} d_{cd}^{\alpha_1} d_{da}^{\alpha_2}}{(\omega_{cb}-\omega_1-\omega_2-\omega_3)(\omega_{db}-\omega_2-\omega_3)(\omega_{ab}-\omega_3)} \right. \\
 & - \frac{d_{ab}^{\alpha_2} d_{bc}^{\mu} d_{cd}^{\alpha_1} d_{da}^{\alpha_3}}{(\omega_{cb}-\omega_1-\omega_2-\omega_3)(\omega_{db}-\omega_2-\omega_3)(\omega_{da}-\omega_3)} + \frac{d_{ab}^{\alpha_3} d_{bc}^{\alpha_2} d_{cd}^{\mu} d_{da}^{\alpha_1}}{(\omega_{dc}-\omega_1-\omega_2-\omega_3)(\omega_{ac}-\omega_2-\omega_3)(\omega_{ab}-\omega_3)} \\
 & - \frac{d_{ab}^{\alpha_1} d_{bc}^{\mu} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{cb}-\omega_1-\omega_2-\omega_3)(\omega_{ca}-\omega_2-\omega_3)(\omega_{da}-\omega_3)} + \frac{d_{ab}^{\alpha_3} d_{bc}^{\alpha_1} d_{cd}^{\mu} d_{da}^{\alpha_2}}{(\omega_{dc}-\omega_1-\omega_2-\omega_3)(\omega_{db}-\omega_2-\omega_3)(\omega_{ab}-\omega_3)} \\
 & \left. + \frac{d_{ab}^{\alpha_2} d_{bc}^{\alpha_1} d_{cd}^{\mu} d_{da}^{\alpha_3}}{(\omega_{dc}-\omega_1-\omega_2-\omega_3)(\omega_{db}-\omega_2-\omega_3)(\omega_{da}-\omega_3)} - \frac{d_{ab}^{\alpha_3} d_{bc}^{\alpha_2} d_{cd}^{\alpha_1} d_{da}^{\mu}}{(\omega_{ad}-\omega_1-\omega_2-\omega_3)(\omega_{ac}-\omega_2-\omega_3)(\omega_{ab}-\omega_3)} \right] \quad (E18)
 \end{aligned}$$

A simpler form of this equation may be obtained by using the symmetrizing operator which takes the sum over all permuted pairs (α_i, ω_i) to combine the eight terms. The placement of the d_{ij}^μ term and the form of the denominator is used to establish the combinations.

The steps are

- (1) Leave the first term alone.
- (2) Combine second, third and fifth term by permuting (α_i, ω_i) to obtain $d_{ab}^{\alpha_1} d_{bc}^{\mu} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}$ product.

This is accomplished for these terms by respectively permuting:

$(\alpha_1, \omega_1) \leftrightarrow (\alpha_3, \omega_3)$ followed by $(\alpha_2, \omega_2) \leftrightarrow (\alpha_3, \omega_3)$; $(\alpha_1, \omega_1) \leftrightarrow (\alpha_2, \omega_2)$; No change. The ω_i in the denominators must also be changed. These terms become

$$\begin{aligned}
& - \frac{\alpha_1 \mu \alpha_2 \alpha_3}{d_{ab} d_{bc} d_{cd} d_{da}} - \frac{\alpha_1 \mu \alpha_2 \alpha_3}{(\omega_{cb} - \omega_1 - \omega_2 - \omega_3)(\omega_{db} - \omega_1 - \omega_3)(\omega_{da} - \omega_3)} \\
& - \frac{\alpha_1 \mu \alpha_2 \alpha_3}{(\omega_{cd} - \omega_1 - \omega_2 - \omega_3)(\omega_{ca} - \omega_2 - \omega_3)(\omega_{da} - \omega_3)} \\
& - \frac{\alpha_1 \mu \alpha_2 \alpha_3}{(\omega_{cd} - \omega_1 - \omega_2 - \omega_3)(\omega_{db} - \omega_1 - \omega_3)(\omega_{ab} - \omega_1)}
\end{aligned} \tag{E19}$$

This can be factored to obtain

$$\begin{aligned}
& - \frac{\alpha_1 \mu \alpha_2 \alpha_3}{(\omega_{cb} - \omega_1 - \omega_2 - \omega_3)} \\
& \left[\frac{1}{(\omega_{ca} - \omega_2 - \omega_3)(\omega_{da} - \omega_3)} + \frac{1}{(\omega_{db} - \omega_1 - \omega_3)} \left(\frac{1}{\omega_{da} - \omega_3} + \frac{1}{\omega_{ab} - \omega_1} \right) \right]
\end{aligned} \tag{E20}$$

The last product reduces to

$$\frac{1}{(\omega_{da} - \omega_3)(\omega_{ab} - \omega_1)} \tag{E21}$$

after using Eq (E13). Equation (E20) factors to

$$- \frac{\alpha_1 \mu \alpha_2 \alpha_3}{(\omega_{cb} - \omega_1 - \omega_2 - \omega_3)(\omega_{da} - \omega_3)} \left[\frac{1}{\omega_{ca} - \omega_2 - \omega_3} + \frac{1}{\omega_{ab} - \omega_1} \right] \tag{E22}$$

The last term in Eq (E22) is

$$\frac{\omega_{cb} - \omega_1 - \omega_2 - \omega_3}{(\omega_{ca} - \omega_2 - \omega_3)(\omega_{ab} - \omega_1)} \tag{E23}$$

Thus Eq (E19) reduces to

$$-\frac{d_{ab}^{\alpha_1} d_{bc}^{\mu} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{ca}-\omega_2-\omega_3)(\omega_{ab}-\omega_1)(\omega_{da}-\omega_3)} \quad (E24)$$

(3) Combine the fourth, sixth and seventh terms of Eq (E18) by permuting (α_i, ω_j) to obtain $d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\mu} d_{da}^{\alpha_3}$ product. This permutation for each term is respectively: $(\alpha_1, \omega_1) \leftrightarrow (\alpha_3, \omega_3)$; $(\alpha_1, \omega_1) \leftrightarrow (\alpha_3, \omega_3)$ followed by $(\alpha_3, \omega_3) \leftrightarrow (\alpha_2, \omega_2)$; $(\alpha_1, \omega_1) \leftrightarrow (\alpha_2, \omega_2)$. After factoring and combining the denominators as above, this procedure yields

$$\frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\mu} d_{da}^{\alpha_3}}{(\omega_{ac}-\omega_1-\omega_2)(\omega_{ab}-\omega_1)(\omega_{da}-\omega_3)} \quad (E25)$$

(4) Permute the eighth term of Eq (E18) by $(\alpha_1, \omega_1) \leftrightarrow (\alpha_3, \omega_3)$ to obtain

$$\frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\alpha_3} d_{da}^{\mu}}{(\omega_{ad}-\omega_1-\omega_2-\omega_3)(\omega_{ac}-\omega_1-\omega_2)(\omega_{ab}-\omega_1)} \quad (E26)$$

Equation (E18) upon substitution of Eqs (E24), (E25) and (E26) then becomes

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) = \frac{1}{3! \hbar^3} \sum_{(\alpha\omega)} \sum_{a,b,c,d} p_{aa}^o$$

$$\left[\frac{d_{ab}^{\mu} d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{ba}-\omega_1-\omega_2-\omega_3)(\omega_{ca}-\omega_2-\omega_3)(\omega_{da}-\omega_3)} - \frac{d_{ab}^{\alpha_1} d_{bc}^{\mu} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{ca}-\omega_2-\omega_3)(\omega_{ab}-\omega_1)(\omega_{da}-\omega_3)} \right] \quad (E27)$$

$$\left. + \frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\mu} d_{da}^{\alpha_3}}{(\omega_{ac}-\omega_1-\omega_2)(\omega_{ab}-\omega_1)(\omega_{da}-\omega_3)} - \frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\alpha_3} d_{da}^{\mu}}{(\omega_{ad}-\omega_1-\omega_2-\omega_3)(\omega_{ac}-\omega_1-\omega_2)(\omega_{ab}-\omega_1)} \right]$$

Equation (E27) may be rewritten by noting $\omega_{ij} = -\omega_{ji}$ and rearranging denominators as

$$\begin{aligned}
 p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) = & - \sum_{(\alpha\omega)} \frac{1}{6\hbar^3} \sum_{a,b,c,d} \rho_{aa}^{\circ} \\
 & \left[\frac{d_{ab}^{\mu} d_{bc}^{\alpha_1} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{ab} + \omega_1 + \omega_2 + \omega_3)(\omega_{ac} + \omega_2 + \omega_3)(\omega_{ad} + \omega_2)} + \frac{d_{ab}^{\alpha_1} d_{bc}^{\mu} d_{cd}^{\alpha_2} d_{da}^{\alpha_3}}{(\omega_{ab} - \omega_1)(\omega_{ac} + \omega_2 + \omega_3)(\omega_{ad} + \omega_3)} \right. \\
 & + \left. \frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\mu} d_{da}^{\alpha_3}}{(\omega_{ab} - \omega_1)(\omega_{ac} - \omega_1 - \omega_2)(\omega_{ad} + \omega_3)} + \frac{d_{ab}^{\alpha_1} d_{bc}^{\alpha_2} d_{cd}^{\alpha_3} d_{da}^{\mu}}{(\omega_{ab} - \omega_1)(\omega_{ac} - \omega_1 - \omega_2)(\omega_{ad} - \omega_1 - \omega_2 - \omega_3)} \right] \quad (E28)
 \end{aligned}$$

Because of the symmetrizing operator $\sum_{(\alpha\omega)}$ this equation will have six terms for each of the terms shown for a total of twenty-four terms with potential resonant denominators.

Butcher (Ref 48:95) extends the above results derived which did not allow for molecular interactions to the case where weak interactions are allowed. If the interaction is strong it must be accounted for in the equation of motion for the density operator and then the derivation of the polarizabilities performed. The effect of the weak interaction is to introduce an uncertainty, Γ_a , into the energy of a state. The transition between two states a and b then has a width $\Gamma_{ab} = \Gamma_a + \Gamma_b = \Gamma_{ba}$. In the presence of weak interactions Eq (E28) becomes

$$\begin{aligned}
p_{\mu\alpha_1\alpha_2\alpha_3}^{(3)}(\omega_1, \omega_2, \omega_3) = & - \sum_{(\alpha\omega)} \frac{1}{6\hbar^3} \sum_{a,b,c,d} \rho_{aa}^o \\
& \left[\frac{\begin{matrix} \mu & \alpha_1 & \alpha_2 & \alpha_3 \\ d_{ab} & d_{bc} & d_{cd} & d_{da} \end{matrix}}{(\omega_{ab} + \omega_1 + \omega_2 + \omega_3 + i\Gamma_{ab})(\omega_{ac} + \omega_2 + \omega_3 + i\Gamma_{ac})(\omega_{ad} + \omega_3 + i\Gamma_{ad})} \right. \\
& + \frac{\begin{matrix} \alpha_1 & \mu & \alpha_2 & \alpha_3 \\ d_{ab} & d_{bc} & d_{cd} & d_{da} \end{matrix}}{(\omega_{ab} - \omega_1 - i\Gamma_{ab})(\omega_{ac} + \omega_2 + \omega_3 + i\Gamma_{ac})(\omega_{ad} + \omega_3 + i\Gamma_{ad})} \\
& + \frac{\begin{matrix} \alpha_1 & \alpha_2 & \mu & \alpha_3 \\ d_{ab} & d_{bc} & d_{cd} & d_{da} \end{matrix}}{(\omega_{ab} - \omega_1 - i\Gamma_{ab})(\omega_{ac} - \omega_1 - \omega_2 - i\Gamma_{ac})(\omega_{ad} - \omega_1 - \omega_2 - \omega_3 - i\Gamma_{ad})} \\
& \left. \right] \quad (E29)
\end{aligned}$$

where the sign on Γ is determined from the causality condition. This third order polarizability and the first order one (Ref 48:95),

$$p_{\mu\alpha}^{(3)}(\omega) = - \frac{1}{\hbar} \sum_{ab} \rho_{aa}^o \frac{d_{ab}^\mu d_{ba}^\alpha}{\omega_{ab} + \omega + i\Gamma_{ab}} + \frac{d_{ab}^\alpha d_{ba}^\mu}{\omega_{ab} - \omega - i\Gamma_{ab}} \quad (E30)$$

provide the complete set of polarizabilities necessary to describe third order processes. It is worth noting that Γ is the linewidth and that only for those cases where a frequency ω_i (or linear combination of frequencies $\sum_i \omega_i$) is close to a transition frequency ω_{ab} does Γ_{ab} become a critical term. For the case where no resonance occurs Γ_{ab} may be ignored with little effect. When all Γ 's can be ignored

the properties of overall permutation symmetry and time reversal symmetry (Ref 48:77-94) then apply. When Γ must be retained, these two properties do not apply. However, since the hamiltonian operator, \hat{H} , used in the derivation of $\hat{\rho}$ and subsequently $\hat{\bar{\rho}}$ represents a dynamical variable invariant under time reversal, $t \rightarrow -t$, it is a real operator in the Schrödinger picture. When \hat{H} is real, the eigenfunctions of \hat{H} are also real. For the case of no d.c. magnetic field, \hat{H} is real and therefore invariant under time reversal (Ref 48:92). A consequence of this condition for \hat{H} is that with real eigenfunctions the dipole matrix element,

$$d_{ab}^\alpha = \langle a | \hat{d}_\alpha | b \rangle \quad (E14)$$

has a useful property. This property is derived as follows

$$(d_{ab}^\alpha)^* = (\langle a | \hat{d}_\alpha | b \rangle)^* = \langle b | \hat{d}_\alpha^* | a \rangle = \langle b | \hat{d}_\alpha | a \rangle = d_{ba}^\alpha \quad (E31)$$

Since the eigenfunction for states a and b are real and \hat{d} is real, Eq (C6),

$$(d_{ab}^\alpha)^* = d_{ab}^\alpha \quad (E32)$$

Equations (E31) and (E32) yield

$$d_{ab}^\alpha = d_{ba}^\alpha \quad (E33)$$

Consequently

$$d_{ab}^\mu d_{ba}^\alpha = d_{ba}^\mu d_{ab}^\alpha = d_{ab}^\alpha d_{ba}^\mu \quad (E34)$$

when there is no dc magnetic field present (the dipole approximation).

Appendix F: $p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}(1)}$ in the Monochromatic Case

In the monochromatic case with no electronic resonances, the dependence of $p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}}$ on $(\omega', \omega'', \omega''')$ will take on a very specific form after the integration over frequency Eq (4.45) is performed.

When the fields are monochromatic; Eq (4.6), this form is

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}}(-\omega_1; -\omega_2, \omega_2, \omega_1) = \frac{p_{00}^0 f_{-\omega_1, \omega_2}^{\mu\alpha_2} f_{\omega_2, -\omega_1}^{*\alpha_1\alpha_3} - p_{11}^0 g_{\omega_1, -\omega_2}^{\alpha_2\mu} g_{-\omega_2, \omega_1}^{*\alpha_3\alpha_1}}{6\hbar^3 (\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10})} \quad (\text{F1})$$

where the f and g factors of Eq (4.56) are given by

$$f_{-\omega_1, \omega_2}^{\mu\alpha_2} = \sum_b \left[\frac{\mu}{d_{ob} d_{b1}} \frac{\alpha_2}{\omega_{bo} - \omega_1} + \frac{\alpha_2 \mu}{d_{ob} d_{b1}} \frac{\mu}{\omega_{bo} + \omega_2} \right] \quad (\text{F2})$$

$$f_{\omega_2, -\omega_1}^{*\alpha_1\alpha_3} = \sum_b \left[\frac{\alpha_1}{d_{ob} d_{b1}} \frac{\alpha_3}{\omega_{bo} + \omega_2} + \frac{\alpha_3 \alpha_1}{d_{ob} d_{b1}} \frac{\alpha_1}{\omega_{bo} - \omega_1} \right]^* \quad (\text{F3})$$

$$g_{\omega_1, -\omega_2}^{\alpha_2\mu} = \sum_b \left[\frac{\alpha_2 \mu}{d_{ob} d_{b1}} \frac{\mu}{\omega_{b1} + \omega_1} + \frac{\mu}{d_{ob} d_{b1}} \frac{\alpha_2}{\omega_{b1} - \omega_2} \right] \quad (\text{F4})$$

$$g_{-\omega_2, \omega_1}^{*\alpha_3\alpha_1} = \sum_b \left[\frac{\alpha_3}{d_{ob} d_{b1}} \frac{\alpha_1}{\omega_{b1} - \omega_2} + \frac{\alpha_1 \alpha_3}{d_{ob} d_{b1}} \frac{\alpha_3}{\omega_{b1} + \omega_1} \right]^* \quad (\text{F5})$$

These equations can be rearranged when the resonance condition of Eq (4.2) is met.

$$\omega_1 - \omega_2 \approx \omega_v \equiv \omega_{10} \quad (4.2)$$

With the definition of ω_{b0} and ω_{b1} , the resonant condition provides

$$\omega_{b0} = \tilde{\omega}_b - \omega_{v0} \quad (F6)$$

$$\omega_{b1} = \tilde{\omega}_b - \tilde{\omega}_v = \tilde{\omega}_b - \tilde{\omega}_{v0} - (\tilde{\omega}_v - \tilde{\omega}_{v0}) \quad (F7)$$

$$\omega_{b1} = \omega_{b0} - \omega_{10} \approx \omega_{b0} - (\omega_1 - \omega_2) \quad (F8)$$

These last results applied to Eq (F2) after a change in the order of the terms, yields

$$f_{-\omega_1, \omega_2}^{\mu\alpha_2} = \sum_b \left[\frac{\alpha_2 \mu}{d_{ob} d_{b1}} \frac{1}{\omega_{b1} + \omega_1 - \omega_2 + \omega_2} + \frac{\mu}{d_{ob} d_{b1}} \frac{\alpha_2}{\omega_{b0} - \omega_1} \right] \quad (F9)$$

$$f_{-\omega_1, \omega_2}^{\mu\alpha_2} = \sum_b \left[\frac{\alpha_2 \mu}{d_{ob} d_{b1}} \frac{1}{\omega_{b1} + \omega_1} + \frac{\mu}{d_{ob} d_{b1}} \frac{\alpha_2}{\omega_{b0} - \omega_1} \right] \quad (F10)$$

This last result, Eq (F10), is proportional to the ordinary Raman scattering (ORS) complex polarizability (Ref 83:114), $p_{\alpha_2 \mu}^{*\omega_1}$

$$f_{-\omega_1, \omega_2}^{\mu\alpha_2} = \hbar p_{\alpha_2 \mu}^{*\omega_1} \quad (F11)$$

Similarly, Eq (F3) becomes

$$f_{-\omega_2, -\omega_1}^{*\alpha_1 \alpha_3} = \sum_b \left[\frac{\alpha_3 \alpha_1}{d_{1b} d_{bo}} \frac{1}{\omega_{b1} + \omega_1 - \omega_2 + \omega_2} + \frac{\alpha_1 \alpha_3}{d_{1b} d_{bo}} \frac{1}{\omega_{bo} - \omega_1} \right] \quad (F12)$$

$$f^{*\alpha_1\alpha_3}_{\omega_2, -\omega_1} = \sum_b \left[\frac{\alpha_3 \alpha_1}{d_{1b} d_{bo}} \frac{d_{1b} d_{bo}}{\omega_{b1} + \omega_1} + \frac{\alpha_1 \alpha_3}{d_{1b} d_{bo}} \frac{d_{1b} d_{bo}}{\omega_{bo} - \omega_1} \right] \quad (F13)$$

This is proportional to the ORS polarizability $p_{\alpha_1\alpha_3}^{\omega_1}$

$$f^{*\alpha_1\alpha_3}_{\omega_2, -\omega_1} = \hbar p_{\alpha_1\alpha_3}^{\omega_1} \quad (F14)$$

For the g factor terms Eq (F3) reduces to

$$g_{\omega_1, -\omega_2}^{\alpha_2\mu} = \sum_b \left[\frac{\alpha_2 \mu}{d_{ob} d_{b1}} \frac{d_{ob} d_{b1}}{\omega_{b1} + \omega_1} + \frac{\mu}{d_{ob} d_{b1}} \frac{\alpha_2}{\omega_{bo} - \omega_1 + \omega_2 - \omega_2} \right] \quad (F15)$$

$$g_{\omega_1, -\omega_2}^{\alpha_2\mu} = \sum_b \left[\frac{\alpha_2 \mu}{d_{ob} d_{b1}} \frac{d_{ob} d_{b1}}{\omega_{b1} + \omega_1} + \frac{\mu}{d_{ob} d_{b1}} \frac{\alpha_2}{\omega_{bo} - \omega_1} \right] \quad (F16)$$

$$g_{\omega_1, -\omega_2}^{\alpha_2\mu} = \hbar p_{\alpha_2\mu}^{*\omega_1} = f_{-\omega_1, \omega_2}^{\mu\alpha_2} \quad (F17)$$

And, from Eq (F5),

$$g_{-\omega_2, \omega_1}^{*\alpha_3\alpha_1} = \sum_b \left[\frac{\alpha_3 \alpha_1}{d_{1b} d_{bo}} \frac{d_{1b} d_{bo}}{\omega_{b1} + \omega_1} + \frac{\alpha_1 \alpha_3}{d_{1b} d_{bo}} \frac{d_{1b} d_{bo}}{\omega_{bo} - \omega_1 + \omega_2 - \omega_2} \right] \quad (F18)$$

$$g_{-\omega_2, \omega_1}^{*\alpha_3\alpha_1} = \sum_b \left[\frac{\alpha_3 \alpha_1}{d_{1b} d_{bo}} \frac{d_{1b} d_{bo}}{\omega_{b1} + \omega_1} + \frac{\alpha_1 \alpha_3}{d_{1b} d_{bo}} \frac{d_{1b} d_{bo}}{\omega_{bo} - \omega_1} \right] \quad (F19)$$

$$g_{-\omega_2, \omega_1}^{*\alpha_3\alpha_1} = \hbar p_{\alpha_1\alpha_3}^{\omega_1} = f^{*\alpha_1\alpha_3}_{\omega_2, -\omega_1} \quad (F20)$$

Thus, for monochromatic fields (or nearly monochromatic fields) with frequency differences very near a Raman active resonance such that Eqs (F6) through (F8) hold, the f and g factors are equal to each other. They are also equal to elements of the ordinary Raman scattering polarizability at the frequency ω_1 . Long (Ref 83) relates these polarizability terms to the Raman scattering cross section in a classical derivation. A similar relation is obtained in this work using a quantum derivation which was presented in Chapter V.

For the multifrequency field case presented here, the equality between the ordinary Raman polarizability and the f and g factors apply only near Raman-type resonances and should therefore be applied with caution. When the relation can be used, however, Eq (4.57) for the third order polarizability simplifies to

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}}(-\omega_1; -\omega_2, \omega_1, \omega_2) = \frac{1}{6\hbar} \frac{(\rho_{00}^0 - \rho_{11}^0)}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}} p_{\alpha_1\alpha_3}^{\omega_1} p_{\alpha_2\mu}^{*\omega_1} \quad (\text{F21})$$

It is important to note that the intensity for ORS and hence the differential scattering cross section depends upon products like $[p_{xy}]x [p_{xy}^*]$. In this product the indices are identical. Thus only when the product in Eq (F21) has the form of $\sum_{\alpha,\beta} [p_{\alpha\beta}] [p_{\alpha\beta}^*]$ will it contain the exact Raman scattering cross section. Under the multifrequency conditions of

$$\begin{aligned} \delta_1 + \delta_1' &\approx 0 \\ \delta_2 + \delta_2' &\sim 0 \quad (10^{-2}\omega_v) \end{aligned} \quad (4.39)$$

the third order polarizabilities derived are near the Raman-type resonance. Therefore, the results obtained here concerning the equality

of the f and g factors may be applied. When this condition fails to hold, the equations for the ORS polarizability are not readily identifiable.

Appendix G: Resonant Polarizability Equations

The expressions for the resonant polarizabilities derived using the approach of Chapter IV are presented for each of the central frequencies $\omega_1, \omega_2, \omega_3$ and ω_4 . These are given in four tables that follow:

- (1) Multifrequency and multiresonant, $f \neq g$
- (2) Multifrequency and multiresonant with Raman Polarizability,
 $f = g$
- (3) Monochromatic and single resonance, $f = g$
- (4) Monochromatic and single resonance with Raman polarizability,
 $f = g$

Table G I

Polarizabilities for Multifrequency and Multiresonance

$$\omega_1 - \delta_1' \leq \omega \leq \omega_1 + \delta_1'$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v, J} \frac{1}{\omega_{v'vJ} - \omega' - \omega'' - i\Gamma_{v'vJ}}$$

$$\times [\rho_v^0 f_{-\omega, \omega'}^{\mu\alpha_2}(v) f_{-\omega', \omega''}^{*\alpha_1\alpha_3}(v) - \rho_v^0 g_{\omega, -\omega''}^{\alpha_2\mu}(v') g_{\omega', \omega''}^{*\alpha_3\alpha_1}(v')]_J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v, J} \frac{1}{\omega_{v'vJ} + \omega' + \omega'' + i\Gamma_{v'vJ}}$$

$$\times [\rho_v^0 f_{\omega', \omega''}^{\alpha_1\alpha_2}(v) f_{-\omega, -\omega''}^{*\mu\alpha_3}(v) - \rho_v^0 g_{-\omega', -\omega''}^{\alpha_2\alpha_1}(v') g_{-\omega, \omega''}^{*\alpha_3\mu}(v')]_J$$

$$+ \frac{[\rho_v^0 f_{-\omega, \omega'}^{\mu\alpha_2}(v) f_{-\omega', -\omega''}^{*\alpha_1\alpha_3}(v) - \rho_v^0 g_{\omega, -\omega'}^{\alpha_2\mu}(v') g_{\omega', \omega''}^{*\alpha_3\alpha_1}(v')]}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}_J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v, J} \frac{1}{\omega_{v'vJ} + \omega' + \omega''' + i\Gamma_{v'vJ}}$$

$$\times [\rho_v^0 f_{\omega', \omega''}^{\alpha_1\alpha_3}(v) f_{\omega, -\omega''}^{*\mu\alpha_2}(v) - \rho_v^0 g_{-\omega', -\omega''}^{\alpha_3\alpha_1}(v') g_{-\omega, \omega''}^{*\alpha_2\mu}(v')]_J$$

Table G I (Continued)

$$\omega_1 - \delta_1' \leq \omega \leq \omega_1 + \delta_1'$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3 v, J} \sum_{\omega_{v'vJ}} \frac{1}{\omega_{v'vJ} - \omega' - \omega'' - i\Gamma_{v'vJ}}$$

$$\times [\rho_v^0 f_{-\omega, \omega'''}^{\mu\alpha_3}(v) f_{-\omega', -\omega''}^{*\alpha_1\alpha_2}(v) - \rho_{v'}^0 g_{\omega, -\omega'''}^{\alpha_3\mu}(v') g_{\omega', \omega''}^{*\alpha_2\alpha_1}(v')]_J$$

$$+ \frac{[\rho_v^0 f_{-\omega, \omega''}^{\mu\alpha_2}(v) f_{-\omega', -\omega''}^{*\alpha_1\alpha_3}(v) - \rho_{v'}^0 g_{\omega, -\omega''}^{\alpha_2\mu}(v') g_{\omega', \omega'''}^{*\alpha_3\alpha_1}(v')]_J}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3 v, J} \sum_{\omega_{v'vJ}} \frac{1}{\omega_{v'vJ} + \omega' + \omega''' + i\Gamma_{v'vJ}}$$

$$\times [\rho_v^0 f_{\omega', \omega'''}^{\alpha_1\alpha_3}(v) f_{\omega, -\omega''}^{*\mu\alpha_2}(v) - \rho_{v'}^0 g_{-\omega', -\omega''}^{\alpha_3\alpha_1}(v') g_{-\omega, \omega''}^{*\alpha_2\mu}(v')]_J$$

TABLE G II
 Polarizabilities for Multifrequency
 and Multiresonance (Raman Polarizability)

$$\omega_1 - \delta\tilde{\Gamma} \leq \omega \leq \omega_1 + \delta\tilde{\Gamma} \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v,J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}]_J}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = \sum_{v,J} \frac{(\rho_v^0 - \rho_{v'}^0)_J}{6\hbar}$$

$$\left[\frac{p_{\mu\alpha_3}^{\omega'''} p_{\alpha_2\alpha_1}^{*\omega}}{\omega_{v'v} + \omega' + \omega'' + i\Gamma_{v'v}} + \frac{p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}}{\omega_{v'v} - \omega' - \omega''' - i\Gamma_{v'v}} \right]_J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v,J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\mu\alpha_2}^{\omega''} p_{\alpha_3\alpha_1}^{*\omega'}]_J}{\omega_{v'vJ} + \omega' + \omega''' + i\Gamma_{v'vJ}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''') = \sum_{v,J} \frac{(\rho_v^0 - \rho_{v'}^0)}{6\hbar}$$

$$\left[\frac{p_{\alpha_1\alpha_2}^{\omega''} p_{\alpha_3\mu}^{*\omega}}{\omega_{v'v} - \omega' - \omega'' - i\Gamma_{v'v}} + \frac{p_{\alpha_1\alpha_3}^{\omega''} p_{\alpha_2\mu}^{*\omega}}{\omega_{v'v} - \omega' - \omega''' - i\Gamma_{v'v}} \right]_J$$

TABLE G II (Continued)

$$\omega_1 - \delta_{\bar{1}'} \leq \omega \leq \omega_1 + \delta_{\bar{1}} \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v,j} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\mu\alpha_2}^{\omega''} p_{\alpha_3\alpha_1}^{*\omega'}]_j}{\omega_v v j + \omega' + \omega''' + i\Gamma_v v j}$$

where $p_{ij}^\omega = p_{ij}^\omega(v, v')$

Table G III
Polarizabilities for Monochromatic and
Single Resonance ($f = g$)

$$\omega = \omega_1$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}} (-\omega_1; -\omega_2, \omega_2, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f^{\mu\alpha_2} f^{*\alpha_1\alpha_3}}{-\omega_1, \omega_2 \quad \omega_2, -\omega_1} \\ \frac{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}}{}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}} (-\omega_1; -\omega_1, \omega_2, \omega_3) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3}$$

$$\left[\frac{f^{\alpha_1\alpha_2} f^{*\mu\alpha_3}}{-\omega_1, \omega_2 \quad \omega_1, -\omega_3} + \frac{f^{\mu\alpha_2} f^{*\alpha_1\alpha_3}}{-\omega_1, \omega_2 \quad \omega_1, -\omega_3} \right] \\ \frac{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}}{+ \frac{\omega_{10} + \omega_1 - \omega_3 - i\Gamma_{10}}{}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}} (-\omega_1; -\omega_3, \omega_3, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f^{\alpha_1\alpha_3} f^{*\mu\alpha_2}}{-\omega_3, \omega_1 \quad \omega_1, -\omega_3} \\ \frac{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}}{}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}} (-\omega_1; -\omega_4, \omega_2, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3}$$

$$\left[\frac{f^{\mu\alpha_3} f^{*\alpha_1\alpha_2}}{-\omega_1, \omega_2 \quad \omega_4, -\omega_2} + \frac{f^{\mu\alpha_2} f^{*\alpha_1\alpha_3}}{-\omega_1, \omega_2 \quad +\omega_4, -\omega_2} \right] \\ \frac{\omega_{10} + \omega_4 - \omega_2 - i\Gamma_{10}}{+ \frac{\omega_{10} + \omega_4 - \omega_2 - i\Gamma_{10}}{}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_1; -\omega_2, \omega_3, \omega_4) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f^{\alpha_1\alpha_3} f^{*\mu\alpha_2}}{-\omega_2, \omega_4 \quad \omega_1, -\omega_3} \\ \frac{\omega_{10} - \omega_2 + \omega_4 + i\Gamma_{10}}{}$$

Table G IV
 Polarizabilities for Monochromatic and
 Single Resonance (Raman Polarizability)

$$\omega = \omega_1 \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}} (-\omega_1; -\omega_2, \omega_2, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\alpha_1\alpha_3}^{\omega_1} p_{\alpha_2\mu}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}} (-\omega_1; -\omega_1, \omega_2, \omega_3) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \times \left[\frac{p_{\mu\alpha_3}^{\omega_3} p_{\alpha_2\alpha_1}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} + \frac{p_{\alpha_1\alpha_3}^{\omega_3} p_{\alpha_2\mu}^{*\omega_1}}{\omega_{10} + \omega_1 - \omega_3 - i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}} (-\omega_1; -\omega_3, \omega_3, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\mu\alpha_2}^{\omega_3} p_{\alpha_3\alpha_1}^{*\omega_3}}{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}} (-\omega_1; -\omega_4, \omega_2, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \times \left[\frac{p_{\alpha_1\alpha_2}^{\omega_2} p_{\alpha_3\mu}^{*\omega_1}}{\omega_{10} + \omega_4 - \omega_2 - i\Gamma_{10}} + \frac{p_{\alpha_1\alpha_3}^{\omega_2} p_{\alpha_2\mu}^{*\omega_1}}{\omega_{10} + \omega_4 - \omega_2 - i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_1; -\omega_2, \omega_3, \omega_4) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\mu\alpha_2}^{\omega_3} p_{\alpha_3\alpha_1}^{*\omega_2}}{\omega_{10} + \omega_4 - \omega_2 + i\Gamma_{10}}$$

Table G V
Polarizabilities for Multifrequency and Multiresonance

$$\omega_2 - \delta_2' \leq \omega \leq \omega_2 + \delta_2'$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v, J} \frac{1}{\omega_{v'vJ} + \omega' + \omega'' + i\Gamma_{v'vJ}}$$

$$\times [\rho_v^0 f_{\omega', \omega'''}^{\alpha_1\alpha_3}(v) f_{\omega, -\omega'''}^{*\mu\alpha_2}(v) - \rho_v^0 g_{-\omega', -\omega'''}^{\alpha_3\alpha_1}(v') g_{-\omega, \omega'''}^{*\alpha_2\mu}(v')]_J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v, J} \frac{1}{\omega_{v'vJ} + \omega' + \omega'' + i\Gamma_{v'vJ}}$$

$$\times [\rho_v^0 f_{\omega', \omega'''}^{\alpha_1\alpha_3}(v) f_{\omega, -\omega'''}^{*\mu\alpha_2}(v) - \rho_v^0 g_{-\omega', -\omega'''}^{\alpha_3\alpha_1}(v') g_{-\omega, \omega'''}^{*\alpha_2\mu}(v')]_J$$

$$+ \frac{[\rho_v^0 f_{\omega', \omega'''}^{\alpha_1\alpha_2}(v) f_{\omega, -\omega'''}^{*\mu\alpha_3}(v) - \rho_v^0 g_{-\omega', -\omega'''}^{\alpha_2\alpha_1}(v) g_{-\omega, \omega'''}^{*\alpha_3\mu}(v')]}{\omega_{v'vJ} + \omega' + \omega'' + i\Gamma_{v'vJ}}_J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v, J} \frac{1}{\omega_{v'vJ} + \omega' + \omega'' + i\Gamma_{v'vJ}}$$

$$[\rho_v^0 f_{\omega', \omega'''}^{\alpha_1\alpha_2}(v) f_{\omega, -\omega'''}^{*\mu\alpha_3}(v) - \rho_v^0 g_{-\omega', -\omega'''}^{\alpha_2\alpha_1}(v) g_{-\omega, \omega'''}^{*\alpha_3\mu}(v')]_J$$

$$+ \frac{[\rho_v^0 f_{-\omega, \omega'''}^{\mu\alpha_2}(v) f_{-\omega', -\omega'''}^{*\alpha_1\alpha_3}(v) - \rho_v^0 g_{\omega, -\omega'''}^{\alpha_2\mu}(v') g_{\omega', \omega'''}^{*\alpha_3\alpha_1}(v')]}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}_J$$

Table G V (Continued)

$$\omega_2 - \delta_2' \leq \omega \leq \omega_2 + \delta_2'$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3 v, J} \sum_{\omega'} \frac{1}{v' v J - \omega' - \omega''' - i\Gamma_{v' v J}}$$

$$\times [\rho_v^0 f_{-\omega, \omega'}^{\mu\alpha_2}(v) f_{-\omega', -\omega'''}^{*\alpha_1\alpha_3}(v) - \rho_{v'}^0 g_{\omega, -\omega'''}^{\alpha_2\mu}(v') g_{\omega', \omega'''}^{*\alpha_3\alpha_1}(v')] J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-SS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3 v, J} \sum_{\omega'} \frac{1}{v' v J - \omega' - \omega''' - i\Gamma_{v' v J}}$$

$$\times [\rho_v^0 f_{-\omega, \omega'}^{\mu\alpha_2}(v) f_{-\omega', -\omega'''}^{*\alpha_1\alpha_3}(v) - \rho_{v'}^0 g_{\omega, -\omega'''}^{\alpha_2\mu}(v') g_{\omega', \omega'''}^{*\alpha_3\alpha_1}(v')] J$$

TABLE G VI
 Polarizabilities for Multifrequency and
 Multiresonance (Raman Polarizability)

$$\omega_2 - \delta_2' \leq \omega \leq \omega_2 + \delta_2' \quad (f = g)$$

$$SRS-S \quad p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v,J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\mu\alpha_2}^{\omega''} p_{\alpha_3\alpha_1}^{*\omega'}]_J}{\omega_{v'vJ} + \omega' + \omega''' + i\Gamma_{v'vJ}}$$

$$CARS \quad p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \sum_{v,J} \frac{(\rho_v^0 - \rho_{v'}^0)}{6\hbar} \left[\frac{p_{\mu\alpha_2}^{\omega''} p_{\alpha_3\alpha_1}^{*\omega'}}{\omega_{v'v} + \omega' + \omega''' + i\Gamma_{v'v}} + \frac{p_{\mu\alpha_3}^{\omega'''} p_{\alpha_2\alpha_1}^{*\omega'}}{\omega_{v'v} + \omega' + \omega'' + i\Gamma_{v'v}} \right]_J$$

$$CSRS \quad p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \sum_{v,J} \frac{(\rho_v^0 - \rho_{v'}^0)}{6\hbar} \left[\frac{p_{\mu\alpha_3}^{\omega'''} p_{\alpha_2\alpha_1}^{*\omega'}}{\omega_{v'v} + \omega' + \omega'' + i\Gamma_{v'v}} + \frac{p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}}{\omega_{v'v} - \omega' - \omega''' - i\Gamma_{v'v}} \right]_J$$

$$CMRS \quad p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v,J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}]_J}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}$$

$$SRS-SS \quad p_{\mu\alpha_1\alpha_2\alpha_3}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v,J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}]_J}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}$$

where $p_{ij}^\omega = p_{ij}^\omega(v, v')$

Table G VII
Polarizabilities for Monochromatic and
Single Resonance ($f = g$)

$$\omega = \omega_2$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}} (-\omega_2; -\omega_1, \omega_1, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f_{-\omega_1, \omega_2}^{\alpha_1\alpha_3} f_{\omega_2, -\omega_1}^{*\mu\alpha_2}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}} (-\omega_2; -\omega_3, \omega_1, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \left[\frac{f_{-\omega_3, \omega_1}^{\alpha_1\alpha_3} f_{\omega_2, -\omega_1}^{*\mu\alpha_2}}{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}} + \frac{f_{-\omega_3, \omega_1}^{\alpha_1\alpha_2} f_{\omega_2, -\omega_1}^{*\mu\alpha_3}}{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}} (-\omega_2; -\omega_2, \omega_4, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \left[\frac{f_{-\omega_2, \omega_4}^{\alpha_1\alpha_2} f_{\omega_2, -\omega_1}^{*\mu\alpha_3}}{\omega_{10} - \omega_2 + \omega_4 + i\Gamma_{10}} + \frac{f_{-\omega_2, \omega_4}^{\mu\alpha_2} f_{\omega_2, -\omega_1}^{*\alpha_1\alpha_3}}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_2; -\omega_1, \omega_4, \omega_3) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f_{-\omega_2, \omega_4}^{\mu\alpha_2} f_{\omega_1, -\omega_3}^{*\alpha_1\alpha_3}}{\omega_{10} - \omega_3 + \omega_1 - i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-SS}} (-\omega_2; -\omega_4, \omega_4, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f_{-\omega_2, \omega_4}^{\mu\alpha_2} f_{\omega_4, -\omega_2}^{*\alpha_1\alpha_3}}{\omega_{10} - \omega_2 + \omega_4 + i\Gamma_{10}}$$

Table G VIII
Polarizabilities for Monochromatic and
Single Resonance (Raman Polarizability)

$$\omega = \omega_2 \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-S}} (-\omega_2; -\omega_1, \omega_1, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\mu\alpha_2}^{\omega_1} p_{\alpha_3\alpha_1}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}} (-\omega_2; -\omega_3, \omega_1, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar}$$

$$\times \left[\frac{p_{\mu\alpha_2}^{\omega_1} p_{\alpha_3\alpha_1}^{*\omega_3}}{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}} + \frac{p_{\mu\alpha_3}^{\omega_1} p_{\alpha_2\alpha_1}^{*\omega_3}}{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}} (-\omega_2; -\omega_2, \omega_4, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar}$$

$$\times \left[\frac{p_{\mu\alpha_3}^{\omega_1} p_{\alpha_2\alpha_1}^{*\omega_2}}{\omega_{10} - \omega_2 + \omega_4 + i\Gamma_{10}} + \frac{p_{\alpha_1\alpha_3}^{\omega_1} p_{\alpha_2\mu}^{*\omega_2}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_2; -\omega_1, \omega_4, \omega_3) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\alpha_1\alpha_3}^{\omega_3} p_{\alpha_2\mu}^{*\omega_2}}{\omega_{10} - \omega_3 + \omega_1 - i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-SS}} (-\omega_2; -\omega_4, \omega_4, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\alpha_1\alpha_3}^{\omega_2} p_{\alpha_2\mu}^{*\omega_2}}{\omega_{10} - \omega_2 + \omega_4 - i\Gamma_{10}}$$

Table G IX

Polarizabilities for Multifrequency and Multiresonance

$$\omega_3 - \delta_3' \leq \omega \leq \omega_3 + \delta_3'$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v,J} \frac{1}{\omega_{vvJ} - \omega' - \omega'' - i\Gamma_{vvJ}}$$

$$\times [\rho_v^0 f_{-\omega, \omega'''}^{\mu\alpha_3}(v) f_{-\omega', -\omega'''}^{*\alpha_1\alpha_2}(v) - \rho_v^0 g_{\omega, -\omega'''}^{\alpha_3\mu}(v') g_{\omega', \omega'''}^{*\alpha_2\alpha_1}(v')] J$$

$$+ \frac{[\rho_v^0 f_{-\omega, \omega'''}^{\mu\alpha_2}(v) f_{-\omega', -\omega'''}^{*\alpha_1\alpha_3}(v) - \rho_v^0 g_{\omega, -\omega'''}^{\alpha_2\mu}(v') g_{\omega', \omega'''}^{*\alpha_3\alpha_1}(v')]}{\omega_{vvJ} - \omega' - \omega''' - i\Gamma_{vvJ}} J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v,J} \frac{1}{\omega_{vvJ} - \omega' - \omega''' - i\Gamma_{vvJ}}$$

$$\times [\rho_v^0 f_{-\omega, \omega'''}^{\mu\alpha_2}(v) f_{-\omega', -\omega'''}^{*\alpha_1\alpha_3}(v) - \rho_v^0 g_{\omega, -\omega'''}^{\alpha_2\mu}(v') g_{\omega', \omega'''}^{*\alpha_3\alpha_1}(v')] J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar^3} \sum_{v,J} \frac{1}{\omega_{vvJ} - \omega' - \omega''' - i\Gamma_{vvJ}}$$

$$\times [\rho_v^0 f_{-\omega, \omega'''}^{\mu\alpha_2}(v) f_{-\omega', -\omega'''}^{*\alpha_1\alpha_3}(v) - \rho_v^0 g_{\omega, -\omega'''}^{\alpha_2\mu}(v') g_{\omega', \omega'''}^{*\alpha_3\alpha_1}(v')] J$$

TABLE G X
 Polarizabilities for Multifrequency and
 Multiresonance (Raman Polarizability)

$$\omega_3 - \delta\hat{\zeta}' \leq \omega \leq \omega_3 + \delta\hat{\zeta}' \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = \sum_{v, J} \frac{(\rho_v^0 - \rho_{v'}^0)}{6\hbar} \\ \times \left[\frac{p_{\alpha_1\alpha_2}^{\omega''} p_{\alpha_3\mu}^{*\omega}}{\omega_{v'v} - \omega' - \omega'' - i\Gamma_{v'v}} + \frac{p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}}{\omega_{v'v} - \omega' - \omega''' - i\Gamma_{v'v}} \right]_J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v, J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}]_J}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v, J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\alpha_1\alpha_3}^{\omega'''} p_{\alpha_2\mu}^{*\omega}]_J}{\omega_{v'vJ} - \omega' - \omega''' - i\Gamma_{v'vJ}}$$

where $p_{ij}^\omega = p_{ij}^\omega(v, v')$

Table G XI
 Polarizabilities for Monochromatic and
 Single Resonance ($f = g$)

$$\omega = \omega_3$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}} (-\omega_3; -\omega_2, \omega_1, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \times \left[\frac{f_{-\omega_3, \omega_1}^{\mu\alpha_3} f_{\omega_2, -\omega_1}^{*\alpha_1\alpha_2}}{\omega_{10}^{-\omega_1+\omega_2-i\Gamma_{10}}} + \frac{f_{-\omega_3, \omega_1}^{\mu\alpha_2} f_{\omega_2, -\omega_1}^{*\alpha_1\alpha_3}}{\omega_{10}^{-\omega_1+\omega_2-i\Gamma_{10}}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}} (-\omega_3; -\omega_1, \omega_1, \omega_3) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f_{-\omega_3, \omega_1}^{\mu\alpha_2} f_{\omega_1, -\omega_3}^{*\alpha_1\alpha_3}}{\omega_{10}^{-\omega_3+\omega_1-i\Gamma_{10}}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_3; -\omega_4, \omega_1, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f_{-\omega_3, \omega_1}^{\mu\alpha_2} f_{\omega_4, -\omega_2}^{*\alpha_1\alpha_3}}{\omega_{10}^{-\omega_2+\omega_4-i\Gamma_{10}}}$$

Table G XII
 Polarizabilities for Monochromatic and
 Single Resonance (Raman Polarizability)

$$\omega = \omega_3 \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CARS}} (-\omega_3; -\omega_2, \omega_1, \omega_1) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar}$$

$$\times \left[\frac{p_{\alpha_1\alpha_2}^{\omega_1} p_{\alpha_3\mu}^{*\omega_3}}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}} + \frac{p_{\alpha_1\alpha_3}^{\omega_1} p_{\alpha_2\mu}^{*\omega_3}}{\omega_{10} - \omega_1 + \omega_2 - i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-P}} (-\omega_3; -\omega_1, \omega_1, \omega_3) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\alpha_1\alpha_3}^{\omega_3} p_{\alpha_2\mu}^{*\omega_3}}{\omega_{10} - \omega_3 + \omega_1 - i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_3; -\omega_4, \omega_1, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\alpha_1\alpha_3}^{\omega_2} p_{\alpha_2\mu}^{*\omega_3}}{\omega_{10} - \omega_2 + \omega_4 - i\Gamma_{10}}$$

Table G XIII
Polarizabilities for Multifrequency and Multiresonance

$$\omega_4 - \delta_4' \leq \omega \leq \omega_4 + \delta_4'$$

$$\begin{aligned}
 & \text{CSRS} \\
 p_{\mu\alpha_1\alpha_2\alpha_3}^{(\text{CSRS})}(-\omega; \omega', \omega'', \omega''') = & \frac{1}{6\hbar^3 v, J} \sum_{\omega} \frac{1}{v' v J + \omega' + \omega'' + i\Gamma} \\
 & \times [\rho_v^0 f_{\omega', \omega'''}^{\alpha_1\alpha_3}(v) f_{\omega, -\omega'''}^{*\mu\alpha_2}(v) - \rho_v^0 g_{-\omega', -\omega'''}^{\alpha_3\alpha_1}(v') g_{-\omega, \omega'''}^{*\alpha_2\mu}(v')] J \\
 & + \frac{[\rho_v^0 f_{\omega', \omega''}^{\alpha_1\alpha_2}(v) f_{\omega, -\omega''}^{*\mu\alpha_3}(v) - \rho_v^0 g_{-\omega', -\omega''}^{\alpha_2\alpha_1}(v') g_{-\omega, \omega''}^{*\alpha_3\mu}(v')]}{v' v J + \omega' + \omega'' + i\Gamma} J \\
 & \text{CMRS} \\
 p_{\mu\alpha_1\alpha_2\alpha_3}^{(\text{CMRS})}(-\omega; \omega', \omega'', \omega''') = & \frac{1}{6\hbar^3 v, J} \sum_{\omega} \frac{1}{v' v J + \omega' + \omega'' + i\Gamma} \\
 & \times [\rho_v^0 f_{\omega', \omega''}^{\alpha_1\alpha_2}(v) f_{\omega, -\omega''}^{*\mu\alpha_3}(v) - \rho_v^0 g_{-\omega', -\omega''}^{\alpha_2\alpha_1}(v') g_{-\omega, \omega''}^{*\alpha_3\mu}(v')] J \\
 & \text{SRS-SS} \\
 p_{\mu\alpha_1\alpha_2\alpha_3}^{(\text{SRS-SS})}(-\omega; \omega', \omega'', \omega''') = & \frac{1}{6\hbar^3 v, J} \sum_{\omega} \frac{1}{v' v J + \omega' + \omega'' + i\Gamma} \\
 & \times [\rho_v^0 f_{\omega', \omega'''}^{\alpha_1\alpha_3}(v) f_{\omega, -\omega'''}^{*\mu\alpha_2}(v) - \rho_v^0 g_{-\omega', -\omega'''}^{\alpha_3\alpha_1}(v') g_{-\omega, \omega'''}^{*\alpha_2\mu}(v')] J
 \end{aligned}$$

TABLE G XIV
 Polarizabilities for Multifrequency and
 Multiresonance (Raman Polarizability)

$$\omega_4 - \delta_4' \leq \omega \leq \omega_4 + \delta_4' \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''') = \sum_{v, J} \frac{(\rho_v^0 - \rho_{v'}^0)}{6\hbar} \\ \times \left[\frac{p_{\mu\alpha_2}^{\omega''} p_{\alpha_3\alpha_1}^{*\omega'}}{\omega_{vv} + \omega' + \omega''' + i\Gamma_{vv}} + \frac{p_{\mu\alpha_3}^{\omega'''} p_{\alpha_2\alpha_1}^{*\omega'}}{\omega_{v'v} + \omega' + \omega'' + i\Gamma_{v'v}} \right] J$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v, J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\mu\alpha_3}^{\omega'''} p_{\alpha_2\alpha_1}^{*\omega'}] J}{\omega_{v'vJ} + \omega' + \omega'' + i\Gamma_{v'vJ}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-SS}}(-\omega; \omega', \omega'', \omega''') = \frac{1}{6\hbar} \sum_{v, J} \frac{[(\rho_v^0 - \rho_{v'}^0) p_{\mu\alpha_2}^{\omega''} p_{\alpha_3\alpha_1}^{*\omega'}] J}{\omega_{v'vJ} + \omega' + \omega''' + i\Gamma_{v'vJ}}$$

where $p_{ij}^\omega = p_{ij}^\omega(v, v')$

Table G XV
Polarizabilities for Monochromatic and
Single Resonance ($f = g$)

$$\omega = \omega_4$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}} (-\omega_4; -\omega_1, \omega_2, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3}$$

$$\times \left[\frac{f_{-\omega_1, \omega_2}^{\alpha_1\alpha_3} f_{\omega_4, -\omega_2}^{*\mu\alpha_2}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} + \frac{f_{-\omega_1, \omega_2}^{\alpha_1\alpha_2} f_{\omega_4, -\omega_2}^{*\mu\alpha_3}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_4; -\omega_3, \omega_1, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f_{-\omega_3, \omega_1}^{\alpha_1\alpha_2} f_{\omega_4, -\omega_2}^{*\mu\alpha_3}}{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-SS}} (-\omega_4; -\omega_2, \omega_2, \omega_4) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar^3} \frac{f_{-\omega_2, \omega_4}^{\alpha_1\alpha_3} f_{\omega_4, -\omega_2}^{*\mu\alpha_2}}{\omega_{10} - \omega_2 + \omega_4 + i\Gamma_{10}}$$

Table G XVI

Polarizabilities for Monochromatic and
Single Resonance (Raman Polarizability)

$$\omega = \omega_4 \quad (f = g)$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CSRS}} (-\omega_4; -\omega_1, \omega_2, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar}$$

$$\times \left[\frac{p_{\mu\alpha_2}^{\omega_2} p_{\alpha_3\alpha_1}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} + \frac{p_{\mu\alpha_3}^{\omega_2} p_{\alpha_2\alpha_1}^{*\omega_1}}{\omega_{10} - \omega_1 + \omega_2 + i\Gamma_{10}} \right]$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{CMRS}} (-\omega_4; -\omega_3, \omega_1, \omega_2) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\mu\alpha_3}^{\omega_2} p_{\alpha_2\alpha_1}^{*\omega_3}}{\omega_{10} - \omega_3 + \omega_1 + i\Gamma_{10}}$$

$$p_{\mu\alpha_1\alpha_2\alpha_3}^{\text{SRS-SS}} (-\omega_4; -\omega_2, \omega_2, \omega_4) = \frac{(\rho_{00}^0 - \rho_{11}^0)}{6\hbar} \frac{p_{\mu\alpha_2}^{\omega_2} p_{\alpha_3\alpha_1}^{*\omega_2}}{\omega_{10} - \omega_2 + \omega_4 + i\Gamma_{10}}$$

Appendix H: Coordinate Rotations

The transformation of a rotating molecular coordinate system, I, to a fixed laboratory system, L, can be carried out by a series of rotations starting out about the laboratory coordinates. Similarly, those quantities that transform as coordinates may be expressed in either coordinate system by use of a rotation transformation matrix. The Euler angles selected are θ , ϕ and ψ (Ref 92:285). The transformation from the I coordinates to L coordinates is obtained by:

(1) A rotation of angle ϕ about the laboratory axis Z to produce X' , Y' , and $Z' = Z$ where $0 \leq \phi \leq 2\pi$. The matrix representing this rotation, $R_1(\phi)$, is

$$R_1(\phi) = \begin{bmatrix} \cos \phi & \sin \phi & 0 \\ -\sin \phi & \cos \phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (H1)$$

(2) Next, a rotation about the Y' axis by an angle θ to produce X'' , $Y'' = Y'$ and $Z'' = Z'$ where $0 \leq \theta \leq \pi$. This rotation matrix, $R_2(\theta)$, is

$$R_2(\theta) = \begin{bmatrix} \cos \theta & 0 & -\sin \theta \\ 0 & 1 & 0 \\ \sin \theta & 0 & \cos \theta \end{bmatrix} \quad (H2)$$

(3) Finally, a rotation by an angle, ψ , about the Z'' axis to give x , y , and $z = Z''$ where $0 \leq \psi \leq 2\pi$. The rotation matrix, $R_3(\psi)$, is

$$R_3(\psi) = \begin{bmatrix} \cos \psi & \sin \psi & 0 \\ -\sin \psi & \cos \psi & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (H3)$$

The combined rotations through the angles ϕ , θ and ψ to obtain the desired coordinate transformation from the laboratory to the molecular coordinates is obtained by the product

$$R = R_3(\psi) R_2(\theta) R_1(\phi) \quad (H4)$$

The matrix multiplication is performed using Eqs (H1), (H2) and (H3) to yield

$$R = \begin{bmatrix} \cos \theta \cos \phi \cos \psi & \cos \theta \sin \phi \cos \psi & -\sin \theta \cos \psi \\ -\sin \phi \sin \psi & +\cos \phi \sin \psi & 0 \\ -\cos \theta \cos \phi \sin \psi & -\cos \theta \sin \phi \sin \psi & -\sin \theta \sin \psi \\ -\sin \phi \cos \psi & +\cos \phi \cos \psi & 0 \\ \sin \theta \cos \phi & \sin \theta \sin \phi & \cos \theta \end{bmatrix} \quad (H5)$$

The coordinate transformation is then

$$\bar{x} = R \bar{X} \quad (H6)$$

where

$$\bar{x} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad \text{and} \quad \bar{X} = \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad (H7)$$

A quantity that transforms as X would be obtained in x by

$$\bar{a} = R \bar{A} \quad (H8)$$

Since the inverse of R (denoted by R^{-1}) exists

$$R^{-1} R = E = R R^{-1} \quad (H9)$$

where E is the unity matrix. Then from Eq (H8)

$$R^{-1} \bar{a} = R^{-1} R \bar{A} = E \bar{A} = \bar{A} \quad (H10)$$

or

$$\bar{A} = R^{-1} \bar{a} \quad (H11)$$

But the matrix R is unitary and

$$R^{-1} = R^T \quad (H12)$$

so that

$$\bar{A} = R^T \bar{a} \quad (H13)$$

An alternative expression to Eq (H8) is to write

$$a_\mu = R_\mu^U A_u = \sum_{u=1}^3 R_\mu^U A_u \quad (H14)$$

In this notation, the greek index represents the molecular coordinates while the english index represents the laboratory coordinates.

The lower index on R_μ^U indicates the row in R and the upper index the column, $R_{\text{row}}^{\text{column}}$. Equation (H13) can be written as

$$A_u = (R^T)_u^\mu a_\mu \quad (H15)$$

But

$$(R^T)_u^\mu = R_\mu^U \quad (H16)$$

so that

$$A_u = R_\mu^U a_\mu \quad (H17)$$

Appendix I: Orientational Averaging

The average of the dipole moment can be reduced to a consideration of the average polarizability. Equation (6.10) shows that the polarizability in a laboratory coordinate frame can be defined as

$$p_{uabc} = (R^T)_u^\mu (R^T)_a^\alpha (R^T)_b^\beta (R^T)_c^\gamma p_{\mu\alpha\beta\gamma} \quad (I1)$$

where Eq (H16) has been used to obtain the rotation matrix elements.

The orientational averaging of this polarizability may be written as

$$\bar{p}_{uabc} = \overline{(R^T)_u^\mu (R^T)_a^\alpha (R^T)_b^\beta (R^T)_c^\gamma} p_{\mu\alpha\beta\gamma} \quad (I2)$$

where $p_{\mu\alpha\beta\gamma}$ is independent of average orientation when it is evaluated in a coordinate system fixed to the molecule. Thus, the average polarizability which depends on the average of the rotation matrix elements, Eq (H5), determines the average dipole moment. The average of the rotation elements can be evaluated by considering the form of the polarizability and using the matrix elements of R^T . The average for both the first and third order polarizability is obtained here under the assumption of random orientation

$$\bar{C} = \frac{1}{8\pi^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_0^{2\pi} d\psi f(\theta, \phi, \psi) C(\theta, \phi, \psi) \quad (I3)$$

with

$$f(\theta, \phi, \psi) = \sin \theta \quad (I4)$$

The first order polarizability is a second order tensor, $p_{\mu\alpha}$,

which is assumed to be evaluated in a molecule fixed coordinate system (greek indices). The polarizability may be transformed to a laboratory coordinate system by

$$p_{ua} = (R^T)_u^\mu (R^T)_a^\alpha p_{\mu\alpha} \quad (I5)$$

which is similar to the third order relation of Eq (I1). The average is then

$$\bar{p}_{ua} = \overline{(R^T)_u^\mu (R^T)_a^\alpha p_{\mu\alpha}} \quad (I6)$$

Since $p_{\mu\alpha}$ is a constant, it can be formed from two constant vectors, \bar{A} and \bar{B} , of arbitrary orientation in the molecular system.

$$p_{\mu\alpha} = A_\mu B_\alpha \quad (I7)$$

But, the average of $p_{\mu\alpha}$ is invariant and linear in both A_μ and B_α . The only invariant of \bar{A} and \bar{B} is $\bar{A} \cdot \bar{B}$. Thus

$$\bar{p}_{ua} = \overline{k_1(\bar{A} \cdot \bar{B})} = \overline{k_1(A_\mu B_\alpha \delta_{\mu\alpha})} \quad (I8)$$

where k_1 is a constant to be determined. It is assumed that there is no symmetry axis for rotation so that no components (e.g., A_1 and B_1) are invariants. This is appropriate for a gas of random orientation. If crystals were being considered, then axial symmetry would have to be taken into account when determining the invariant quantities. Similarly, the average in the laboratory coordinate system may be written as

$$\overline{\overline{p}_{ua}} = \overline{k_2(\bar{A} \cdot \bar{B})} = \overline{k_2(A_u B_a \delta_u^a)} \quad (I9)$$

where k_2 is a constant. The two values of Eqs (I8) and (I9) must be equal under proper averaging. Thus

$$\overline{k_2(A_u B_a \delta_u^a)} = \overline{k_1(A_\mu B_\alpha \delta_\mu^\alpha)} \quad (I10)$$

or with Eq (H15)

$$\overline{k_2(R^T)_u^\mu A_\mu (R^T)_a^\alpha B_\alpha \delta_u^a} = \overline{k_1 A_\mu B_\alpha \delta_\mu^\alpha} \quad (I11)$$

After dividing by k_2 and multiplying by δ_u^a this becomes

$$\overline{(R^T)_u^\mu (R^T)_a^\alpha A_\mu B_\alpha} = C \delta_\mu^\alpha \delta_u^a A_\mu B_\alpha \quad (I12)$$

But \bar{A} and \bar{B} were chosen to be constants independent of the average, so they can be eliminated from both sides of the equation with the result

$$\overline{(R^T)_u^\mu (R^T)_a^\alpha} = C \delta_\mu^\alpha \delta_u^a \quad (I13)$$

The constant C can now be evaluated from specific elements of R^T using Eq (H5).

$$\overline{(R^T)_3^3 (R^T)_3^3} = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \cos^2 \theta \sin \theta = \frac{1}{3} \quad (I14)$$

$$\overline{(R^T)_2^3 (R^T)_2^3} = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin^3 \theta \sin^2 \phi = \frac{1}{3} \quad (I15)$$

Thus $C = 1/3$. The correctness of Eq (I13) may be checked further by considering

$$\overline{(R^T)_2^3 (R^T)_3^3} = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \cos \theta \sin^2 \theta \sin \phi = 0 \quad (I16)$$

The final result of the averaged rotation matrix for the first order polarisability is

$$\overline{(R^T)_u^\mu (R^T)_a^\alpha} = \frac{1}{3} \delta_u^\alpha \delta_u^\alpha \quad (I17)$$

The third order polarisability $p_{\mu\alpha\beta\gamma}$ which is a constant in the molecular system may be constructed from four arbitrary constant vectors \bar{A} , \bar{B} , \bar{C} and \bar{D} . This polarisability may then be written as

$$p_{\mu\alpha\beta\gamma} = A_\mu B_\alpha C_\beta D_\gamma \quad (I18)$$

The invariants of these vectors are $(\bar{A} \cdot \bar{B})$, $(\bar{A} \cdot \bar{C})$, $(\bar{A} \cdot \bar{D})$, $(\bar{B} \cdot \bar{C})$, $(\bar{B} \cdot \bar{D})$ and $(\bar{C} \cdot \bar{D})$ again assuming no symmetry axes are present for rotation. The invariant nature of the average of $p_{\mu\alpha\beta\gamma}$ taking into account the quadralinear dependence of $p_{\mu\alpha\beta\gamma}$ on the vectors can be expressed as

$$\overline{p_{\mu\alpha\beta\gamma}} = k_1 (\bar{A} \cdot \bar{B})(\bar{C} \cdot \bar{D}) + k_2 (\bar{A} \cdot \bar{C})(\bar{B} \cdot \bar{D}) + k_3 (\bar{A} \cdot \bar{D})(\bar{B} \cdot \bar{C}) \quad (I19)$$

or

$$\overline{p_{\mu\alpha\beta\gamma}} = k_1 (A_\mu B_\alpha \delta_\mu^\alpha)(C_\beta D_\gamma \delta_\beta^\gamma) + k_2 (A_\mu C_\beta \delta_\mu^\beta)(B_\alpha D_\gamma \delta_\alpha^\gamma) + k_3 (A_\mu D_\gamma \delta_\mu^\gamma)(B_\alpha C_\beta \delta_\beta^\beta) \quad (I20)$$

$$\bar{p}_{\mu\alpha\beta\gamma} = (k_1 \delta_{\mu}^{\alpha} \delta_{\beta}^{\gamma} + k_2 \delta_{\mu}^{\beta} \delta_{\alpha}^{\gamma} + k_3 \delta_{\mu}^{\gamma} \delta_{\alpha}^{\beta}) \overline{A_{\mu} B_{\alpha} C_{\beta} D_{\gamma}} \quad (I21)$$

Similarly, the average in a laboratory coordinate system may be written as

$$\bar{p}_{uabc} = (k_4 \delta_u^a \delta_b^c + k_5 \delta_u^b \delta_a^c + k_6 \delta_u^c \delta_a^b) \overline{A_u B_a C_b D_c} \quad (I22)$$

where the k_i 's are constants to be determined. Equation (I22) may be rewritten as

$$\begin{aligned} \bar{p}_{uabc} = & (k_4 \delta_u^a \delta_b^c + k_5 \delta_u^b \delta_a^c + k_6 \delta_u^c \delta_a^b) \\ & \times \overline{(R^T)_u^{\mu} (R^T)_a^{\alpha} (R^T)_b^{\beta} (R^T)_c^{\gamma} A_{\mu} B_{\alpha} C_{\beta} D_{\gamma}} \end{aligned} \quad (I23)$$

In both Eqs (I21) and (I23), $A_{\mu} B_{\alpha} C_{\beta} D_{\gamma}$ are constants independent of the orientational averaging process. Since these two equations represent the same quantity after averaging, they may be set equal

$$(k_1 \delta_u^a \delta_b^c + k_2 \delta_u^b \delta_a^c + k_3 \delta_u^c \delta_a^b) \bar{v}_{uabc}^{\mu\alpha\beta\gamma} = (k_4 \delta_u^a \delta_b^c + k_5 \delta_u^b \delta_a^c + k_6 \delta_u^c \delta_a^b) \quad (I24)$$

where

$$\bar{v}_{uabc}^{\mu\alpha\beta\gamma} = \overline{(R^T)_u^{\mu} (R^T)_a^{\alpha} (R^T)_b^{\beta} (R^T)_c^{\gamma}} \quad (I25)$$

and $A_{\mu} B_{\alpha} C_{\beta} D_{\gamma}$ have been eliminated from both sides of the equation.

Equation (I24) may be rewritten as

$$\bar{v}_{uabc}^{\mu\alpha\beta\gamma} = (a_1 \delta_a^u \delta_c^b + a_2 \delta_b^u \delta_c^a + a_3 \delta_c^u \delta_b^a) (k_1 \delta_{\mu}^{\alpha} \delta_{\beta}^{\gamma} + k_2 \delta_{\mu}^{\beta} \delta_{\alpha}^{\gamma} + k_3 \delta_{\mu}^{\gamma} \delta_{\alpha}^{\beta}) \quad (I26)$$

where a_i is the new constant resulting from the k_i 's. Expanding Eq (I26) one gets

$$\begin{aligned} V_{uabc}^{\mu\alpha\beta\gamma} &= C_{11} \delta_{\mu\beta\alpha c}^{\alpha\gamma ub} + C_{21} \delta_{\mu\alpha\alpha c}^{\beta\gamma ub} + C_{31} \delta_{\mu\alpha\alpha c}^{\gamma\beta ub} \\ &+ C_{12} \delta_{\mu\beta b c}^{\alpha\gamma ua} + C_{22} \delta_{\mu\alpha b c}^{\beta\gamma ua} + C_{32} \delta_{\mu\alpha b c}^{\gamma\beta ua} \\ &+ C_{13} \delta_{\mu\beta c b}^{\alpha\gamma ua} + C_{23} \delta_{\mu\alpha c b}^{\beta\gamma ua} + C_{33} \delta_{\mu\alpha c b}^{\gamma\beta ua} \end{aligned} \quad (I27)$$

where

$$\delta_{ijk1}^{mnop} = \delta_i^m \delta_j^n \delta_k^o \delta_1^p \quad (I28)$$

The C_{ij} are new constants to be determined using the matrix elements of the rotation matrix, Eq (H5). In performing the calculation of the average $V_{uabc}^{\mu\alpha\beta\gamma}$ for a specified set of indices, Eq (I3) and (I4) are used. Also, many of the averages with different indices are the same permitting the selection of the one most easily integrated. For example

$$V_{3333}^{3333} = \sum_{i,j} C_{ij} = C_1 \quad (I29)$$

and

$$V_{3333}^{3333} = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \cos^4 \theta \sin \theta = \frac{1}{5} \quad (I30)$$

but C_1 is also equal to any V where all of the upper indices are the same and all of the lower indices are the same (e.g.,

$C_1 = V_{2222}^{3333} = V_{1111}^{3333}$). A check of C_1 can then be performed by

$$V_{1111}^{3333} = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin^5 \theta \cos^4 \theta = \frac{1}{5} \quad (I31)$$

This value of C_1 will be used to check the values of the other C_{ij} 's later. Now

$$C_{11} = V_{1122}^{1122} = V_{1133}^{3311} = V_{3322}^{2233} \quad (I32)$$

The last two averages in Eq (I32) are used to obtain C_{11} and to check the value

$$V_{1133}^{3311} = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin^5 \theta \cos^2 \phi \cos^2 \psi = \frac{2}{15} \quad (I33)$$

$$V_{3322}^{2233} = \frac{1}{8\pi^2} \int_0^{2\pi} d\psi \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin^5 \theta \sin^2 \phi \sin^2 \psi = \frac{2}{15} \quad (I34)$$

Thus, the value of C_{11} is

$$C_{11} = \frac{2}{15} \quad (I35)$$

Repeating this procedure for the remainder of the C_{ij} 's yields the following results

$$\begin{aligned} V_{uabc}^{\mu\alpha\beta\gamma} = & \frac{2}{15} \delta_{\mu\beta\alpha c}^{\alpha\gamma ub} - \frac{1}{30} \delta_{\mu\alpha\alpha c}^{\beta\gamma ub} - \frac{1}{30} \delta_{\mu\alpha\alpha c}^{\gamma\beta ub} \\ & - \frac{1}{30} \delta_{\mu\beta b c}^{\alpha\gamma ua} + \frac{2}{15} \delta_{\mu\alpha b c}^{\beta\gamma ua} - \frac{1}{30} \delta_{\mu\alpha b c}^{\gamma\beta ua} \\ & - \frac{1}{30} \delta_{\mu\beta c b}^{\alpha\gamma ua} - \frac{1}{30} \delta_{\mu\alpha c b}^{\beta\gamma ua} + \frac{2}{15} \delta_{\mu\alpha c b}^{\gamma\beta ua} \end{aligned} \quad (I36)$$

From the definition of Eq (I28) and after factoring, Eq (I36) becomes

$$\begin{aligned}
 \overline{(R^T)_u^\mu (R^T)_a^\alpha (R^T)_b^\beta (R^T)_c^\gamma} &= \frac{1}{30} \delta_a^u \delta_c^b (4\delta_\mu^\alpha \delta_\beta^\gamma - \delta_\mu^\beta \delta_\alpha^\gamma - \delta_\mu^\gamma \delta_\alpha^\beta) \\
 &\quad - \frac{1}{30} \delta_b^u \delta_c^a (\delta_\mu^\alpha \delta_\beta^\gamma - 4\delta_\mu^\beta \delta_\alpha^\gamma + \delta_\mu^\gamma \delta_\alpha^\beta) \\
 &\quad - \frac{1}{30} \delta_c^u \delta_b^a (\delta_\mu^\alpha \delta_\beta^\gamma + \delta_\mu^\beta \delta_\alpha^\gamma - 4\delta_\mu^\gamma \delta_\alpha^\beta) \\
 &= \overline{R_\mu^u R_\alpha^a R_\beta^b R_\gamma^c} \tag{I37}
 \end{aligned}$$

This result can be checked by using Eq (I29)

$$C_1 = \sum_{i,j} C_{ij}$$

$$\text{where } C_1 = \frac{1}{5}$$

From the sum of the coefficients in Eq (I36)

$$\sum_{i,j} C_{ij} = \frac{1}{5}$$

The result is in agreement with that of Monson and McClain (Ref 93:31).

Appendix J: Third Order Polarizations

The third order vector polarizations for the processes SRS-S, CARS, SRS-P CSRS, CMRS and SRS-SS determined by the method of Chapter VII, are presented in these tables. The format is to supply in tabular form for each frequency, ω_1 , ω_2 , ω_3 , and ω_4 the third order susceptibilities (x_{1122}^i , x_{1212}^i and x_{1221}^i), the vector elements, v_I (in the form $(\hat{a}_{II} \cdot \hat{a}_{III}) \hat{a}_I^*$), the field magnitude $\epsilon_I^* \epsilon_{II} \epsilon_{III}$, and the multiplicative coefficient (K) for the equation

$$\begin{aligned}
 P_i(\omega) = & \sum_t K \int_{-\infty}^{\infty} d\omega' d\omega'' d\omega''' \left\{ \left[x_{1122}^i(-\omega; \omega', \omega'', \omega''') + x_{1122}^{NR} \right]_t v_I \right. \\
 & + \left[x_{1212}^i(-\omega; \omega', \omega'', \omega''') + x_{1212}^{NR} \right]_t v_{II} \\
 & + \left[x_{1221}^i(-\omega; \omega', \omega'', \omega''') + x_{1221}^{NR} \right]_t v_{III} \\
 & \left. \times \epsilon_I^*(\omega') \epsilon_{II}(\omega'') \epsilon_{III}(\omega''') \delta(\omega - \omega' - \omega'' - \omega''') \right\} \quad (J1)
 \end{aligned}$$

where t is the set of transitions under consideration and is determined by the quantum number set $(v, J \rightarrow v', J')$. ω is defined to be the sum $(\omega' + \omega'' + \omega''')$.

Table J I

Third Order Polarization at $\omega_1 - \delta_1' \leq \omega \leq \omega_1 + \delta_1'$

$$1. \text{ SRS-S } (\omega_1) : \epsilon_2^* (-\omega') \epsilon_2(\omega'') \epsilon_1(\omega''') : K = 6$$

$$x_{1122}^{\text{SRS-S}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6hD} \frac{1}{45} [3\gamma_s^2(\omega''', \omega) - 5\delta^2 s(\omega''', \omega)]_t$$

$$x_{1212}^{\text{SRS-S}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6hD} \frac{1}{45} [45a_s^2(\omega''', \omega) - 2\gamma_s^2(\omega''', \omega)]_t$$

$$x_{1221}^{\text{SRS-S}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6hD} \frac{1}{45} [3\gamma_s^2(\omega''', \omega) + 5\delta^2 s(\omega''', \omega)]_t$$

$$v_I = (\hat{a}_2 \cdot \hat{a}_1) \hat{a}_2^* : v_{II} = (\hat{a}_2^* \cdot \hat{a}_1) \hat{a}_2 : v_{III} = (\hat{a}_2^* \cdot \hat{a}_2) \hat{a}_1$$

$$D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J I (Continued)

Third Order Polarization at $\omega_1 - \delta_1' \leq \omega \leq \omega_1 + \delta_1'$

$$2. \text{ CARS } (\omega_1) : \epsilon_1^* (-\omega') \epsilon_2(\omega'') \epsilon_3(\omega''') : K = 6$$

$$\begin{aligned} x_{1122}^{\text{CARS}} (-\omega; \omega', \omega'', \omega''') &= \frac{n\Delta_t}{6h} \frac{1}{45D_1} [3\gamma_c^2 (\omega''', -\omega') - 5\delta_c^2 (\omega''', -\omega')]_t \\ &\quad + \frac{1}{45D_2} [3\gamma_c^2 (\omega''', \omega) - 5\delta_c^2 (\omega''', \omega)]_t \end{aligned}$$

$$\begin{aligned} x_{1212}^{\text{CARS}} (-\omega; \omega', \omega'', \omega''') &= \frac{n\Delta_t}{6h} \frac{1}{45D_1} [3\gamma_c^2 (\omega''', -\omega') + 5\delta_c^2 (\omega''', -\omega')]_t \\ &\quad + \frac{1}{45D_2} [45a_c^2 (\omega''', \omega) - 2\gamma_c^2 (\omega''', \omega)]_t \end{aligned}$$

$$\begin{aligned} x_{1221}^{\text{CARS}} (-\omega; \omega', \omega'', \omega''') &= \frac{n\Delta_t}{6h} \frac{1}{45D_1} [45a_c^2 (\omega''', -\omega') - 2\gamma_c^2 (\omega''', -\omega')]_t \\ &\quad + \frac{1}{45D_2} [3\gamma_c^2 (\omega''', \omega) + 5\delta_c^2 (\omega''', \omega)]_t \end{aligned}$$

$$v_I = (\hat{a}_2 \cdot \hat{a}_3) \hat{a}_1^* : v_{II} = (\hat{a}_1^* \cdot \hat{a}_3) \hat{a}_2 : v_{III} = (\hat{a}_1^* \cdot \hat{a}_2) \hat{a}_3$$

$$D_1 = (\omega_t + \omega' + \omega'' + i\Gamma_t) : D_2 = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J I (Continued)

Third Order Polarization at $\omega_1 - \delta_1' \leq \omega \leq \omega_1 + \delta_1'$

3. SRS-P (ω_1) : $\varepsilon_3^*(-\omega')\varepsilon_3(\omega'')\varepsilon_1(\omega''')$: K = 6

$$x_{1122}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [3\gamma_p^2(\omega'', -\omega') - 5\delta_p^2(\omega'', -\omega')]_t$$

$$x_{1212}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [45a_p^2(\omega'', -\omega') - 2\gamma_p^2(\omega'', -\omega')]_t$$

$$x_{1221}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [3\gamma_p^2(\omega'', -\omega') + 5\delta_p^2(\omega'', -\omega')]_t$$

$$V_I = (\hat{a}_3 \cdot \hat{a}_1) \hat{a}_3^* : V_{II} = (\hat{a}_3^* \cdot \hat{a}_1) \hat{a}_3 : V_{III} = (\hat{a}_3^* \cdot \hat{a}_3) \hat{a}_1$$

$$D = (\omega_t + \omega' + \omega''' + i\Gamma_t)$$

4. CSRS (ω_1) : $\varepsilon_4^*(-\omega')\varepsilon_2(\omega'')\varepsilon_2(\omega''')$: K = 3

$$x_{1122}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{3\hbar D} \frac{1}{45} [3\gamma_r^2(\omega'', \omega) - 5\delta_r^2(\omega'', \omega)]_t$$

$$x_{1212}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [45a_r^2(\omega'', \omega) + \gamma_r^2(\omega'', \omega) + 5\delta_r^2(\omega'', \omega)]_t$$

$$x_{1221}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''') = x_{1212}^{\text{CSRS}}(-\omega; \omega', \omega'', \omega''')$$

$$V_I = (\hat{a}_2 \cdot \hat{a}_2) \hat{a}_4^* : V_{II} = (\hat{a}_4^* \cdot \hat{a}_2) \hat{a}_2 : V_{III} = (\hat{a}_4^* \cdot \hat{a}_2) \hat{a}_2 = V_{II}$$

$$D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J I (Continued)

Third Order Polarization at $\omega_1 - \delta_1' \leq \omega \leq \omega_1 + \delta_1'$

$$5. \text{ CMRS } (\omega_1) : \varepsilon_2^* (-\omega') \varepsilon_3(\omega'') \varepsilon_4(\omega''') : K = 6$$

$$x_{1122}^{\text{CMRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6hD} \frac{1}{45} [3\gamma_m^2 (\omega'', -\omega') - 5\delta_m^2 (\omega'', -\omega')]_t$$

$$x_{1212}^{\text{CMRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6hD} \frac{1}{45} [45a_m^2 (\omega'', -\omega') - 2\gamma_m^2 (\omega'', -\omega')]_t$$

$$x_{1221}^{\text{CMRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6hD} \frac{1}{45} [3\gamma_m^2 (\omega'', -\omega') + 5\delta_m^2 (\omega'', -\omega')]_t$$

$$V_I = (\hat{a}_3 \cdot \hat{a}_4) \hat{a}_2^* : V_{II} = (\hat{a}_2^* \cdot \hat{a}_4) \hat{a}_3 : V_{III} = (\hat{a}_2^* \cdot \hat{a}_3) \hat{a}_4$$

$$D = (\omega_t + \omega' + \omega''' + i\Gamma_t)$$

Table J II

Third Order Polarization at $\omega_2 - \delta_2' \leq \omega \leq \omega_2 + \delta_2'$

$$1. \text{ SRS-S } (\omega_1) : \epsilon_1^* (-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''') : K = 6$$

$$x_{1122}^{\text{SRS-S}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [3\gamma_s^2 (\omega'', -\omega') - 5\delta_s^2 (\omega'', -\omega')]_t$$

$$x_{1212}^{\text{SRS-S}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [45a_s^2 (\omega'', -\omega') - 2\gamma_s^2 (\omega'', -\omega')]_t$$

$$x_{1221}^{\text{SRS-S}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [3\gamma_s^2 (\omega'', -\omega') + 5\delta_s^2 (\omega'', -\omega')]_t$$

$$V_I = (\hat{a}_1 \cdot \hat{a}_2) \hat{a}_1^* : V_{II} = (\hat{a}_1^* \cdot \hat{a}_2) \hat{a}_1 : V_{III} = (\hat{a}_1^* \cdot \hat{a}_1) \hat{a}_2$$

$$D = (\omega_t + \omega' + \omega''' + i\Gamma_t)$$

$$2. \text{ CARS } (\omega_2) : \epsilon_3^* (-\omega') \epsilon_1(\omega'') \epsilon_1(\omega''') : K = 3$$

$$x_{1122}^{\text{CARS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [3\gamma_c^2 (\omega'', -\omega') - 5\delta_c^2 (\omega'', -\omega')]_t$$

$$x_{1221}^{\text{CARS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} \\ x [45a_c^2 (\omega'', -\omega') + \gamma_c^2 (\omega'', -\omega') + 5\delta_c^2 (\omega'', -\omega')]_t$$

$$x_{1212}^{\text{CARS}} (-\omega; \omega', \omega'', \omega''') = x_{1122}^{\text{CARS}} (-\omega; \omega', \omega'', \omega''')$$

$$V_I = (\hat{a}_1 \cdot \hat{a}_1) \hat{a}_3^* : V_{II} = (\hat{a}_3^* \cdot \hat{a}_1) \hat{a}_1 : V_{III} = (\hat{a}_3^* \cdot \hat{a}_1) \hat{a}_1 = V_{II}$$

$$D = (\omega_t + \omega' + \omega''' + i\Gamma_t)$$

Table J II (Continued)

Third Order Polarization at $\omega_2 - \delta_2 \leq \omega \leq \omega_2 + \delta_2$

$$3. \text{ CSRS } (\omega_2) : \epsilon_2^* (-\omega') \epsilon_4(\omega'') \epsilon_1(\omega''') : K = 6$$

$$\begin{aligned} x_{1122}^{\text{CSRS}} (-\omega; \omega', \omega'', \omega''') &= \frac{n\Delta_t}{6\hbar} \left[\frac{1}{45D_1} [3\gamma_r^2(\omega''', -\omega') - 5\delta_r^2(\omega''', -\omega')]_t \right. \\ &\quad \left. + \frac{1}{45D_2} [3\gamma_r^2(\omega''', \omega) - 5\delta_r^2(\omega''', \omega)]_t \right] \end{aligned}$$

$$\begin{aligned} x_{1212}^{\text{CSRS}} (-\omega; \omega', \omega'', \omega''') &= \frac{n\Delta_t}{6\hbar} \left[\frac{1}{45D_1} [3\gamma_r^2(\omega''', -\omega') + 5\delta_r^2(\omega''', -\omega')]_t \right. \\ &\quad \left. + \frac{1}{45D_2} [45a_r^2(\omega''', \omega) - 2\gamma_r^2(\omega''', \omega)]_t \right] \end{aligned}$$

$$\begin{aligned} x_{1221}^{\text{CSRS}} (-\omega; \omega', \omega'', \omega''') &= \frac{n\Delta_t}{6\hbar} \left[\frac{1}{45D_1} [45a_r^2(\omega''', -\omega') - 2\gamma_r^2(\omega''', -\omega')]_t \right. \\ &\quad \left. + \frac{1}{45D_2} [3\gamma_r^2(\omega''', \omega) + 5\delta_r^2(\omega''', \omega)]_t \right] \end{aligned}$$

$$V_I = (\hat{a}_4 \cdot \hat{a}_1) \hat{a}_2^* : V_{II} = (\hat{a}_2^* \cdot \hat{a}_1) \hat{a}_4 : V_{III} = (\hat{a}_2^* \cdot \hat{a}_4) \hat{a}_1$$

$$D = (\omega_t + \omega' + \omega''' + i\Gamma_t) : D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J II (Continued)

Third Order Polarization at $\omega_2 - \delta_2' \leq \omega \leq \omega_2 + \delta_2'$

4. CMRS (ω_2) : $\epsilon_1^*(-\omega')\epsilon_4(\omega'')\epsilon_3(\omega''')$: $K = 6$

$$x_{1122}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta}{6\hbar D} t \frac{1}{45} [3\gamma_m^2(\omega''', \omega) - 5\delta_m^2(\omega''', \omega)]_t$$

$$x_{1212}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta}{6\hbar D} t \frac{1}{45} [45a_m^2(\omega''', \omega) - 2\gamma_m^2(\omega''', \omega)]_t$$

$$x_{1221}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta}{6\hbar D} t \frac{1}{45} [3\gamma_m^2(\omega''', \omega) + 5\delta_m^2(\omega''', \omega)]_t$$

$$V_I = (\hat{a}_4 \cdot \hat{a}_3) \hat{a}_1^* : V_{II} = (\hat{a}_1^* \cdot \hat{a}_3) \hat{a}_4 : V_{III} = (\hat{a}_1^* \cdot \hat{a}_4) \hat{a}_3$$

$$D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J II (Continued)

Third Order Polarization at $\omega_2 - \delta_2' \leq \omega \leq \omega_2 + \delta_2'$

5. SRS-SS (ω_2) : $\epsilon_4^* (-\omega') \epsilon_4 (\omega'') \epsilon_2 (\omega''')$: $K = 6$

$$x_{1122}^{\text{SRS-SS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6KD} [3\gamma_q^2 (\omega''', \omega) - 5\delta_q^2 (\omega''', \omega)]_t$$

$$x_{1212}^{\text{SRS-SS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6KD} [45a_q^2 (\omega''', \omega) - 2\gamma_q^2 (\omega''', \omega)]_t$$

$$x_{1221}^{\text{SRS-SS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6KD} [3\gamma_q^2 (\omega''', \omega) + 5\delta_q^2 (\omega''', \omega)]_t$$

$$V_I = (\hat{a}_4 \cdot \hat{a}_2) \hat{a}_4^* : V_{II} = (\hat{a}_4^* \cdot \hat{a}_2) \hat{a}_4 : V_{III} = (\hat{a}_4^* \cdot \hat{a}_4) \hat{a}_2$$

$$D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J III

Third Order Polarization at $\omega_3 - \delta\tilde{\omega} \leq \omega \leq \omega_3 + \delta\tilde{\omega}$

1. CARS (ω_3) : $\epsilon_2^*(-\omega')\epsilon_1(\omega'')\epsilon_1(\omega''') : K = 3$

$$x_{1122}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{3MD} \frac{1}{45} [3\gamma_c^2(\omega'', \omega) - 5\delta_c^2(\omega'', \omega)]_t$$

$$x_{1212}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6MD} \frac{1}{45} \\ \times [45a_c^2(\omega'', \omega) + \gamma_c^2(\omega'', \omega) + 5\delta_c^2(\omega'', \omega)]_t$$

$$x_{1221}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''') = x_{1212}^{\text{CARS}}(-\omega; \omega', \omega'', \omega''')$$

$$v_I = (\hat{a}_1 \cdot \hat{a}_1) \hat{a}_2^* : v_{II} = (\hat{a}_2^* \cdot \hat{a}_1) \hat{a}_1 : v_{III} = (\hat{a}_2^* \cdot \hat{a}_1) \hat{a}_1 = v_{II}$$

$$D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

2. SRS-P (ω) : $\epsilon_1^*(-\omega')\epsilon_1(\omega'')\epsilon_3(\omega''') : K = 6$

$$x_{1122}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6MD} \frac{1}{45} [3\gamma_p^2(\omega''', \omega) - 5\delta_p^2(\omega''', \omega)]_t$$

$$x_{1212}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6MD} \frac{1}{45} [45a_p^2(\omega''', \omega) - 2\gamma_p^2(\omega''', \omega)]_t$$

$$x_{1221}^{\text{SRS-P}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6MD} \frac{1}{45} [3\gamma_p^2(\omega''', \omega) + 5\delta_p^2(\omega''', \omega)]_t$$

$$v_I = (\hat{a}_1 \cdot \hat{a}_3) \hat{a}_1^* : v_{II} = (\hat{a}_1^* \cdot \hat{a}_3) \hat{a}_1 : v_{III} = (\hat{a}_1^* \cdot \hat{a}_1) \hat{a}_3$$

$$D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J III (Continued)

Third Order Polarization at $\omega_3 - \delta\hat{\beta}' \leq \omega \leq \omega_3 + \delta\hat{\beta}'$

3. CMRS (ω_3) : $\epsilon_4^*(-\omega')\epsilon_1(\omega'')\epsilon_2(\omega''')$: $K = 6$

$$x_{1122}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta t}{6\kappa D} \frac{1}{45} [3\gamma_m^2(\omega''', \omega) - 5\delta_m^2(\omega''', \omega)]_t$$

$$x_{1212}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta t}{6\kappa D} \frac{1}{45} [45a_m^2(\omega''', \omega) - 2\gamma_m^2(\omega''', \omega)]_t$$

$$x_{1221}^{\text{CMRS}}(-\omega; \omega', \omega'', \omega''') = \frac{n\Delta t}{6\kappa D} \frac{1}{45} [3\gamma_m^2(\omega''', \omega) + 5\delta_m^2(\omega''', \omega)]_t$$

$$v_I = (\hat{a}_1 \cdot \hat{a}_2) \hat{a}_4^* : v_{II} = (\hat{a}_4^* \cdot \hat{a}_2) \hat{a}_1 : v_{III} = (\hat{a}_4^* \cdot \hat{a}_1) \hat{a}_2$$

$$D = (\omega_t - \omega' - \omega''' - i\Gamma_t)$$

Table J IV

Third Order Polarization at $\omega_4 - \delta_4' \leq \omega \leq \omega_4 + \delta_4'$

1. CSRS (ω_4) : $\epsilon_1^* (-\omega') \epsilon_2(\omega'') \epsilon_3(\omega''')$: $K = 3$

$$x_{1122}^{\text{CSRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{3\hbar D} \frac{1}{45} [3\gamma_r^2 (\omega'', -\omega') - 5\delta_r^2 (\omega'', -\omega')]_t$$

$$x_{1212}^{\text{CSRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} \\ \times [45a_r^2 (\omega'', -\omega') + \gamma_r^2 (\omega'', -\omega') + 5\delta_r^2 (\omega'', -\omega')]_t$$

$$x_{1221}^{\text{CSRS}} (-\omega; \omega', \omega'', \omega''') = x_{1212}^{\text{CSRS}} (-\omega; \omega', \omega'', \omega''')$$

$$V_I = (\hat{a}_2 \cdot \hat{a}_2) \hat{a}_1^* : V_{II} = (\hat{a}_1^* \cdot \hat{a}_2) \hat{a}_2 : V_{III} = (\hat{a}_1^* \cdot \hat{a}_2) \hat{a}_2 = V_{II}$$

$$D = (\omega_t + \omega' + \omega'' + i\Gamma_t)$$

2. CMRS (ω_4) : $\epsilon_3^* (-\omega') \epsilon_1(\omega'') \epsilon_2(\omega''')$: $K = 6$

$$x_{1122}^{\text{CMRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [3\gamma_m^2 (\omega''', -\omega') - 5\delta_m^2 (\omega''', -\omega')]_t$$

$$x_{1212}^{\text{CMRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [3\gamma_m^2 (\omega''', -\omega') + 5\delta_m^2 (\omega''', -\omega')]_t$$

$$x_{1221}^{\text{CMRS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta_t}{6\hbar D} \frac{1}{45} [45a_m^2 (\omega'', -\omega') - 2\gamma_m^2 (\omega'', -\omega')]_t$$

$$V_I = (\hat{a}_1 \cdot \hat{a}_2) \hat{a}_3^* : V_{II} = (\hat{a}_3^* \cdot \hat{a}_2) \hat{a}_1 : V_{III} = (\hat{a}_3^* \cdot \hat{a}_1) \hat{a}_2$$

$$D = (\omega_t + \omega' + \omega'' + i\Gamma_t)$$

Table J IV (Continued)

Third Order Polarization at $\omega_4 - \delta_4 \leq \omega \leq \omega_4 + \delta_4$

$$3. \text{ SRS-SS } (\omega_4) : \epsilon_2^* (-\omega') \epsilon_2(\omega'') \epsilon_4(\omega''') : K = 6$$

$$x_{1122}^{\text{SRS-SS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta t}{6MD} \frac{1}{45} [3\gamma_q^2 (\omega'', -\omega') - 5\delta_q^2 (\omega'', -\omega')]_t$$

$$x_{1212}^{\text{SRS-SS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta t}{6MD} \frac{1}{45} [45a_q^2 (\omega'', -\omega') - 2\gamma_q^2 (\omega'', -\omega')]_t$$

$$x_{1221}^{\text{SRS-SS}} (-\omega; \omega', \omega'', \omega''') = \frac{n\Delta t}{6MD} \frac{1}{45} [3\gamma_q^2 (\omega'', -\omega') + 5\delta_q^2 (\omega'', -\omega')]_t$$

$$V_I = (\hat{a}_2 \cdot \hat{a}_4) \hat{a}_2^* : V_{II} = (\hat{a}_2^* \cdot \hat{a}_4) \hat{a}_2 : V_{III} = (\hat{a}_2^* \cdot \hat{a}_2) \hat{a}_4$$

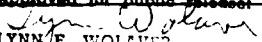
$$D = (\omega_t + \omega' + \omega''' + i\Gamma_t)$$

VITA

Robert I. Weber received his degree in Aeronautical and Astronautical Engineering from The Ohio State University in June of 1961 and entered active duty in the U.S. Air Force shortly thereafter. He subsequently served as a Research Engineer working on magnetohydrodynamic accelerators at Arnold Engineering Development Center, Arnold AFS, Tenn and a Nuclear Weapons Delivery Research Officer at the AF Weapons Laboratory, Kirtland AFB, New Mexico. He received his MS degree in Engineering Physics from the School of Engineering of the Air Force Institute of Technology (AFIT) in June 1966. He was then assigned to the Plasma Physics Laboratory of the Air Force Aerospace Research Laboratories as a Research Scientist and performed experimental and theoretical work on plasma instabilities and electric gas lasers until July 1970. In July 1970 he was assigned to the Electric Laser Section of the AF Weapons Laboratory where he served as a Project Officer and Section Chief. He entered the PhD program of the School of Engineering at AFIT in June of 1975 as a student in Engineering Physics.

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A set of complete and unambiguous third order polarizations were derived for multifrequency (broadband) Coherent Anti-Stokes Raman Scattering (CARS) in molecular gases. The final equations were expressed in a laboratory coordinate frame and were appropriately macroscopic to facilitate the interpretation of experimental results. These polarization equations were made applicable for a general electric field vector polarization and any overlapping distribution of the electric field amplitude in frequency space. The derivation started with the dipole moment approximation and two laser fields as inputs. | | |

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BLOCK 20 (cont)

These two fields, the pump and Stokes fields, had their central frequencies separated by a Raman rotational-vibrational resonant frequency. The generated fields considered were also limited to two; an anti-Stokes and a second Stokes. To more accurately determine the CARS field amplitude, equations were also developed for five related third order nonlinear processes; two parametric (Coherent Stokes Raman Scattering and Coherent Mixed Raman Scattering) and three nonparametric (Stimulated Raman Scattering at the Stokes frequencies). Coherence properties of the fields were not included. The simplification of the general results obtained to the accepted monochromatic equation was noted from the form of the final results.

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